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MEASUREMENT OF REDOX POTENTIAL AND DETERMINATION OF FERROUS IRON IN GROUND WATERS

By

KUSUG KOMOLRIT

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DEPARTMENT OF CIVIL ENGINEERING

UNIVERSITY OF ILLINOIS

URBANA, ILLINOIS

JANUARY, 1962

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I. INTRODUCTION

A. Nature and Importance of the Problem

The problem of iron in water supplies is world wide, but varies considerably in magnitude. In the United States, and particularly in the central states, where deep wells are the source of water for many communities, the problem is especially acute. For example, 70 per cent of the public water supplies in Illinois contain iron in excess of the recommended U. S. Public Health Service limit of 0.3 mg/l. Current data indicates that one-third of those plants having iron removal facilities are not reducing the iron content of the finished water to a satisfactory level (13).

The methods of iron removal have been reviewed adequately in the literature by Applebaum (5), Babcock (7), Fosnot (17), and Nordell (34). The most widely used method for iron removal, which is also regarded as the conventional method, consists of aeration, sedimentation and filtration. This method is more economical than other methods. The principles on which the conventional method is based require that the iron which exists in ground water, mainly in the form of soluble ferrous iron, be converted by oxidation to insoluble forms of ferric iron which can be removed by sedimentation and rapid sand filtration. Hence the success of the treatment will depend very largely on the degree of oxidation attained. However, the mechanisms by which the iron is removed by sand filters are not yet understood. It is assumed that there are three possible mechanisms which may contribute to the overal efficiency of iron removal (13): (a) catalysis by previously deposited material on the filter media; (b) a very long passage and contact time with thin films, which could promote the oxidation reaction;

(c) adsorption and reaction phenomena based on the adsorption of flocs to the sand grains and subsequently oxidation.

Many studies had been performed with and without the use of pilot plants in an attempt to delineate the factors and mechanisms which control the iron removal process. However, many attempts have not succeeded owing to the lack of a reliable method of determining ferrous iron. The determination of ferrous and ferric iron must be reliable so that the state of oxidation of the iron present at any point in the treatment process can be determined with confidence.

The conversion of ferrous iron to ferric iron is an oxidation-reduction reaction. Therefore, the measurement of oxidation-reduction potentials (redox) may help to reveal the reaction phenomena and may also be useful as a possible means of controlling the treatment process, since the relative concentration of oxidants and reductants involved can be measured by determining the prevailing redox potential. One of the great advantages of redox potential measurements, if it can be used as a controlling parameter during treatment, is that the measurements can be accomplished by simple techniques. The measurement depends solely on the use of instrumentation which does not require a highly skilled analyst and can be obtained and installed within a relatively short period of time. It could pave the way for automatic control of water treatment processes involving iron removal in a way similar to its successful application in many waste treatment processes.

B. Purpose of the Study

The present study can be divided into two phases:

1. Determination of the reliable method for the analysis of ferrous iron. Up to the present time, several methods have been proposed

for the determination of iron, and many methods pertaining to the determination of iron have been quite thoroughly summarized in a report presented by Oborn (36). However, almost all of the methods are concerned mainly with the determination of total iron, and they cannot be used to distinguish between the ferrous and ferric forms. It is particularly important to the succeeding work in this study that an accurate and reliable method for ferrous iron determination be selected. The ortho-phenanthroline method given in the 11th Edition of Standard Methods (2) was first selected for the study since it is claimed that for natural and treated waters, the ortho-phenanthroline method has attained the greatest acceptance for reliability (2, 43). The method also can be performed with a relatively simple procedure and can be adapted with ease to field determination. The reliability of the ortho-phenanthroline method was then compared with the 4,7 diphenyl - 1, 10 phenanthroline reagent method or bathophenanthroline method.

The bathophenanthroline method was considered because it is a recently developed method which has been found to give a higher degree of accuracy and sensitivity than the ortho-phenanthroline method (27, 31). However, this method involves a more complicated procedure which cannot be well adapted to field determinations.

Therefore, the scope of the study in this phase has involved the determination of the accuracy and reliability of the ortho-phenanthroline method as compared with the bathophenanthroline method. Some modifications of the ortho-phenanthroline method were investigated in order to adapt it to field application without sacrificing accuracy and reliability.

2. The second phase of the study is devoted to evaluation of redox potential measurement as a parameter determining the efficiency in the iron removal of ground water. Another objective of the survey was to

determine whether there is any relationship between the characteristics of raw water as indicated by the redox potential and other chemical analysis to its treatability with respect to the iron removal. Thirty-one plants in Illinois were selected for this survey study and their locations are shown in Fig. 1.

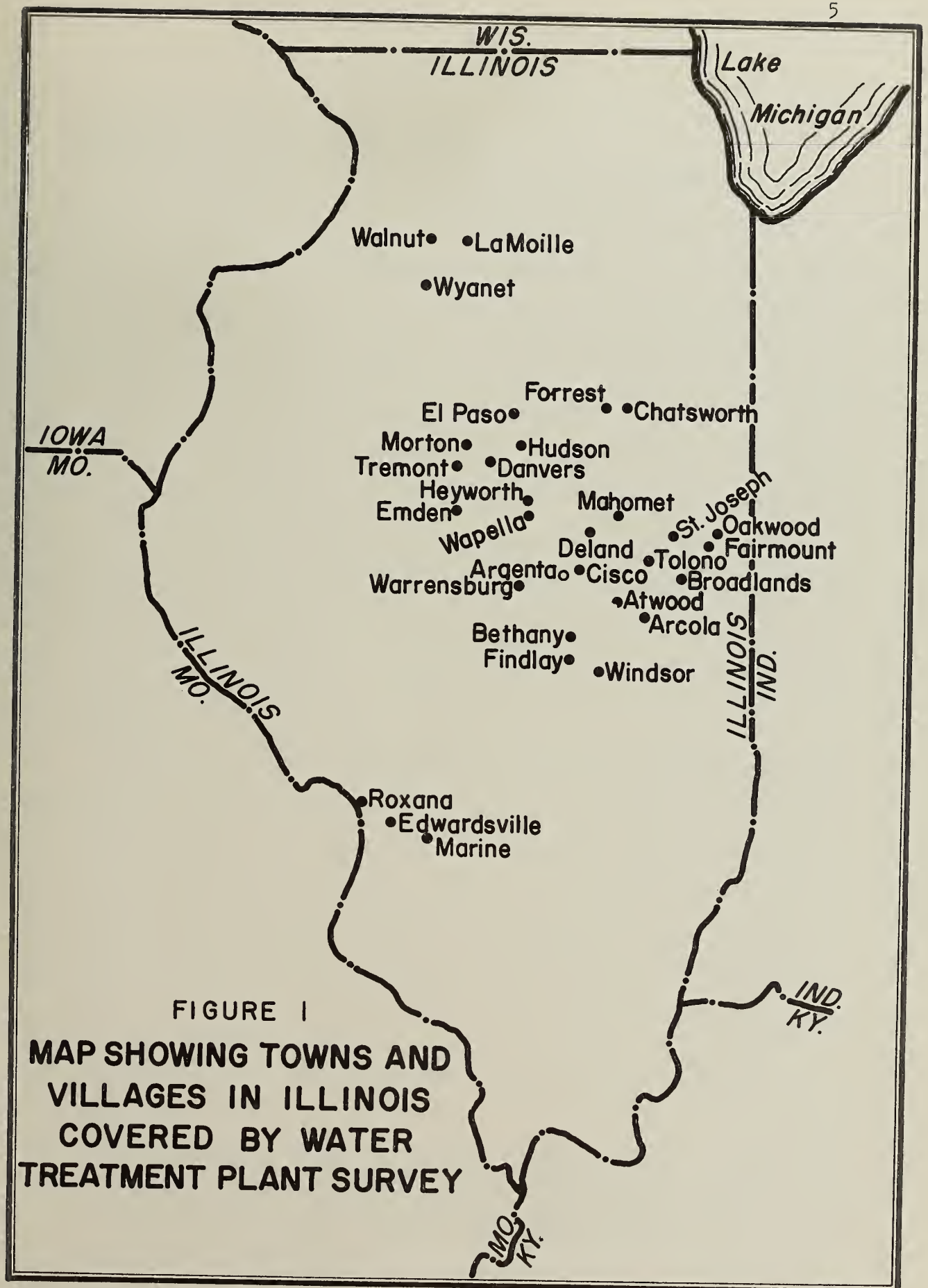

FIGURE 1

MAP SHOWING TOWNS AND VILLAGES IN ILLINOIS COVERED BY WATER TREATMENT PLANT SURVEY

II. HISTORICAL REVIEW

A. Determination of Iron and Ferrous Iron

The methods for determining iron which are in general use can be classified into two types, i.e., volumetric titration and colimetric procedures. The volumetric titration was widely used prior to the development of colorimetric methods about a decade ago. The principles of the titration method are usually based on the chemical reduction of all iron which is present in the solution to the ferrous iron form. This is followed by titration with some oxidizing agents of know concentrations. Numerous oxidizing agents have been used, including MnO_4^{+2}, IO_3^-, $Cr_2O_7^{-2}$, and Ce^{+4}. However, owing to their low sensitivity, these methods are limited to conditions where there are relatively large quantities of ferrous iron and where other reducing agents are absent. Hence they are not applicable to the determination of ferrous iron at the low concentration generally found in the natural waters (31).

Because of their high sensitivity and the ease in performing the analyses, colorimetric procedures have become the most widely used methods for the determination. A variety of color-developing reagents have been used, ranging from thiocyanate, to pyridyls, nitrosophenols and several derivatives of phenanthroline. Some of these common colorimetric reagents with their characteristics have been presented in a table by Sandell (43). However, many of them are limited in their use due to various interferences and the factors which also must be taken into consideration, as Sandell has pointed out,

> "There was no lack of colorimetric reagents for iron, but comparatively few are well suited for the determination of traces of iron. Some reagents react with ferric iron, others with ferrous. The former generally have the

> disadvantage that they cannot be used in the presence of appreciable concentrations of such ions as fluroide and pyrophosphate which form stable complexes with trivalent iron in acid medium, in which the color reaction is carried out. In such cases better results can frequently be obtained by resorting to a reagent reacting with ferrous iron, which does not form such complexes or at least less stable ones."

Among all of the available colorimetric reagents, ortho-phenanthroline has been highly recommended, since it has proved to give very stable color in the determination of total iron (2, 36, 43). The other recommended derivatives of phenanthroline which also are employed include, 2, 2' - bipyridyl and 2, 2', 2" - ter - pyridyl (2, 41). Recently a new method employing the derivative 4,7 - diphenyl-1, 10 - phenanthroline also known as bathophenanthroline has been developed. This new reagent is quite specific and very sensitive to very small amounts of iron. It has been successfully modified to detect the total iron concentration with accuracy up to one part per billion in high purity water (27).

However, it can be noted that most of the methods of determination are primarily concerned with the total iron and do not distinguish between the ferrous or ferric iron forms. Since the ferrous iron is very unstable, it can be oxidized easily in the presence of oxygen as follows:

$$2Fe^{++} + 4\ HCO_3^{-1} + H_2O + \frac{1}{2}\ O_2 \longrightarrow 2F_e\ (OH)_3 + 4\ CO_2$$

If the sample is subjected to a strong reducing environment the reaction is reversed, and the solution may contain large quantities of ferrous iron (41). In the determination of total iron by either ortho-phenanthroline or its derivatives, all iron present in the solution is generally reduced to the ferrous iron form by the use of hydroxylamine reagent (NH_2OH . HCl). If it is desired to determine the amount of ferrous iron in the solution, the reducing agent is then omitted. However, this

method is not very reliable. As pointed out by Lee and Stumm (31), these colorimetric reagents are capable of disturbing the ferrous - ferric equilibrium. There has been difficulties reported concerning the use of these reagents for specific ferrous iron determination, therefore.

Another procedure which also is used for the analytical differentiation of ferrous iron from ferric iron is polarography, but this method is again limited to relatively large concentrations of ferrous iron and cannot be very well applied to the concentrations which are normally found in waters. Cooke and his associates (10) have developed a coulometric titration procedure which is very sensitive to low concentrations of ferrous iron. Titration have been carried out at concentrations as low as one part per billion. However, it requires of special instrumentation which is not normally available.

The 10th Edition Standard Methods (3) has recommended the use of ortho-phenanthroline with sodium acetate buffer as reagents for determining ferrous iron in waters, and only slight modification is made in the 11th Edition (2) by substituting ammonium acetate in place of the sodium acetate. It is claimed that the color developed is stable for several days.

Lee and Stumm (31) noted that when the sample contained less than approximately 1 mg/l ferrous iron in the presence of ferric iron, the color formed was unstable and increased with time. They found 40 to 60 per cent increase in absorbance for various ferrous-ferric mixtures in a period of 30 minutes. From their investigations, they concluded that neither the ortho-phenanthroline procedure nor any of the previously reported procedures are adequate for the reliable determination of ferrous iron in solutions with concentrations less than 1 mg/l ferrous iron. They attributed the failure of the methods to a lack of sensitivity or instability of the developed color.

It was concluded from the investigation that the ortho-phenanthroline method be employed under certain conditions where: 1) 1 mg/l or more of ferrous iron is present in the solution being analyzed; 2) the molar ratio of ortho-phenanthroline to total iron (ferrous plus ferric) exceeds 30; 3) the absorbance measurement is made within 10-15 min. after color formation and 4) the solution is free of interfering materials and protected from direct sunlight. Bathophenanthroline has been recommended as a substitute reagent to overcome these obstacles. The proposed bathophenanthroline procedure primarily follows the method which was developed by Smith and his associates (46) for the determination of total iron. The main modification is the omission of hydroxylamine hydrochloride when the ferrous iron is being determined. From the results of their investigation, they reported that the colorimetric procedure using bathophenanthroline as the color developing reagent had been found to give reliable determinations of ferrous iron in the presence of ferric iron in quantities measured in micrograms. However, they pointed out some of the disadvantages associated with the use of bathophenanthroline, i.e., the relatively high cost of the reagents and elaborate analytical procedure.

B. History and Previous Work on Redox Potentials

The significance of oxidation-reduction as a fundamental ecological factor has long been appreciated by investigators in the realms of physics, chemistry, biochemistry, bacteriology and soil microbiology. According to Glasstone (18), the studies of the oxidation-reduction systems were made by W. D. Bancroft as early as in 1892. Though the practical application of redox potentials have been widely accepted in various fields at the present time, it still has not been fully appreciated due to a number of difficulties which remain unsolved.

Theoretically each and every process involving oxidation-reduction can be monitored by means of continuous redox potential measurement. In the presence of strong oxidants and reductants, the potential measurement can be obtained quite accurately as can be seen from its application to the potentiometric titration, in which the types of the oxidant and the reductant present are known.

In complex systems where a variety of redox components, including some unknown species, are present, the redox potentials measured will represent the gross effects of the redox components in the system. These may only indicate the relative effects of oxidants to reductants. Although the exact interpretation of these types of systems can not be established, the values obtained have been widely applied empirically. In cyanide plating waste treatment (45, 49), for example, redox potential has been used as a control parameter, since it has been found that the cyanide is oxidized to cyanates by chlorine at an approximate redox potential of +150 millivolts. The cyanates are further oxidized to nitrogen gas and carbon dioxide at a potential of approximately +700 millivolts. In the control of bleach manufacture (15, 39), chlorine is added to a caustic solution (NaOH) at a rate controlled by the oxidation-reduction potential which is usually between +500 to +600 millivolts to form bleach. The treatment of toxic hexavalent chromium by reduction to the non-toxic trivalent chromium salts are also controlled by the use of redox potentials (25).

The applicability of redox potential as a control parameter in domestic sewage treatment was also claimed by many investigators e.g., Nussberger (35), Hood and Rohlick (22) in the control of the activated sludge process; and was suggested by Grune and Lotze (19) in the control of sludge digestion.

The applications of redox potential as a ecological parameter in the natural environment have also been studied by many investigators. However, it is often pointed out that the systems in the natural environment usually are poorly poised. Most of those who have made measurements therefore, have come to the conclusion that since they could not obtain reproducible redox potential measurements, their measurements were unreliable. As a result, they often abandoned their investigations (6).

Bass Becking and his associates (6) have accumulated data of redox potential and pH of waters from various environmental sources. They concluded that, at high pH, low redox potentials are more common than at low pH; whereas at low pH very high potentials are obtainable. They also felt that it may be possible to use the relative redox potential and pH as a parameter indicating environmental limits of algae and few groups of bacteria. Pearsall and Mortimer (37) had studied the variation in redox potential with depth in natural waters and muds in relation to the seasonal change, they found that the redox potential of surface water was normally about 0.50 to 0.52 volts, although, during fall overturn, a slightly lower value was obtained. Allgeir and his associates (1) in their study of redox potential and pH of lake waters, recorded values of redox potential ranging from 0.380 to 0.505 volts. Pierce (38) in his investigations found that the redox potential and the dissolved oxygen of ground water appeared to be important parameters in relation to the rate of tree growth. Deficiency of dissolved oxygen and low values of the redox potential were found to correlate with a slow rate of tree growth; such conditions of ground water were unfavorable to the natural reproduction of most upland trees but not swamp species.

In the application of redox potential to measure the corrosiveness of soil by Starkey and Wight (12, 47), it was found that the bacterial

corrosion was most severe when the redox potentials ranged between 0 and 100 mv. The sites at which moderate corrosion occurred had redox potentials ranging between 100 and 200 mv. Well-aerated soils with redox potentials greater than 400 mv. were classed as non-corrosive with respect to bacterial corrosion.

The idea of employing the redox potential as a parameter in the water treatment plant is rather new. In a study of Weart and Margrave (50) in an attempt to explain the variation in performance of iron removal plants in Illinois, they found that a low redox potential in raw well water did not necessarily indicate unsatisfactory plant performance. The response of the water to aeration, as measured by redox potential, was an important consideration. When aeration alone raised the redox potential of a water to a level approaching 244 mv., the plant would function satisfactorily provided reasonable care was given to operation. It was noted that in most plants using bicarbonate waters, containing ammonium but no sulfate, and with a low initial redox reading, the potentials of these waters could not be raised to satisfactory levels with aeration alone. Supplementary treatment with an oxidant such as chlorine had proved to be effective in maintaining oxidizing environment and increasing the efficiency of the process. Weart and Margrave also found that in those plants with satisfactory iron removal, there was no significant shift in the redox potential of water during filtration, even though the dissolved oxygen content was reduced. However, for those plants which showed unsatisfactory performance, the redox potential of the filter effluent reverted towards that of raw well water and the dissolved oxygen originally present in the influent was depleted. Under these conditions, completely anaerobic-conditions existed in the filter, and some ferric iron was reduced to the soluble ferrous state with a resultant

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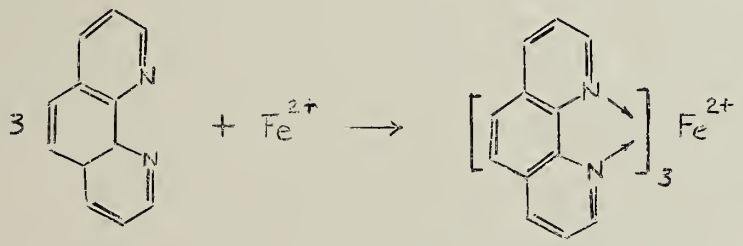
low iron removal efficiency. The investigators set a limit of 100 mv. for raw water, above which iron removal is satisfactory, and below which iron removal is not satisfactory with conventional treatment.

III. THEORETICAL CONSIDERATIONS

A. Principles of Iron Determination by Ortho-phenanthroline.

It has been shown that the chemical reaction in the colorimetric determination of iron by ortho-phenanthroline is based on the chelating action between ortho-phenanthroline and ferrous iron which produces an orange-red color complex. This reaction can be represented by the chemical equation as follows:



(ortho-phenanthroline) (ferrous-orthophenanthroline complex)

From the above chemical equation, it is evident that the two nitrogen atoms in ortho-phenanthroline each have an unshared pair of electrons that can be shared with the ferrous iron. Three such molecules of the organic compound attach themselves to the metallic iron to form a orange-red complex ion. Ferric iron also will form a complex with three molecules of ortho-phenanthroline in a similar manner and give a light blue color (11).

The intensity of color formed varies with the concentration of iron present and follows Beer's Law, provided that the ortho-phenanthroline is in excess. The spectrophotometric determination then can be employed.

The ferrous - ortho-phenanthroline complex which is orange-red in color may change to a blue complex due to the oxidation of ferrous ion to ferric ion.

$$[Ph_3Fe]^{2+} \longrightarrow [Ph_3Fe]^{3+} + e^-$$

Orange-red Light-blue

"Ph" denotes a molecule of ortho-phenanthroline. The complex salt of ferrous and ferric iron also are referred to as "ferrion" and "ferri-in". Upon prolonged standing the blue complex of ferric iron may further change to a yellow-complex which is also produced by complexing ferric iron and ortho-phenanthroline (21).

In the colorimetric determination, there are important factors which also much be considered. Some of these factors are stability of the color developed, interferences by other substances, pH of the solution and the suitable wavelength to be employed in the colorimetric measurement.

According to the kinetic studies on formation and dissociation of ferrous and ferric complexes with ortho-phenanthroline by Kolthoff and his associates (29), the quantitative conversion of ferrous iron to ferrous complex in acid solution is dependent on the ratio of excess ortho-phenanthroline acid. In order that the reaction be 99 percent complete, the ratio of excess (with reference to ferrous iron) ortho-phenanthroline to hydrogen ions must be 0.035 or greater in the equilibrium mixture. Lee and Stumm (31) also pointed out that:

> "Since phenanthroline is a base, it combines with a proton to form phenanthroline ion; therefore, the amount of excess phenantholine necessary is dependent on pH. At a pH of less than approximately 5, the protons in solution compete with the iron for the available positions on the nitrogen atoms of phenanthroline. Therefore, the amount of excess phenanthroline is dependent on the acidity of color formation, particularly at pH values less than 4-5".

As the results of studies by many investigators (16, 20, 33), it has been found that in general the color developed with ortho-phenanthroline is independent of pH in the range between 3 and 8. According to Standard Methods (2), however, a pH between 2.9 and 3.5 insures rapid color development.

Ortho-phenanthroline, as well as various derivatives, also react with a number of metals, particularly the divalent to form colored (e.g., Ni, Co, Cu) or colorless (e.g., Zn) complexes. The presence of any of these metals, although not interfering directly with the color measurement, may

consume reagent which in turn may prevent development of the full color intensity of iron.

According to Sandell (4) who studied various interfering ions and their effect on the iron determination by ortho-phenanthroline:

> "Silver and bismuth give precipitates. Certain divalent metals such as cadmium, mercury, and zinc form slightly soluble complexes with the reagent and, moreover, reduce the intensity of the iron color, but the interference can be diminished by adding a larger excess of reagent. The maximum permissible concentration of these ions for 2 p.p.m. of iron is approximately 50 p.p.m. of Cd, 1 p.p.m. of Hg, and 10 p.p.m. of Zn. Hg^{+} may be present up to 10 p.p.m. (pH 3-9). Beryllium (50 p.p.m.) does not interfere if the pH lies between 3.0 and 5.5; below the former pH a stable complex is formed with the reagent and above the latter pH the hydroxide is precipitated. Mo^{+6} does not interfere above pH 5.5, but in more acid solutions it gives a turbidity. Tungstate decreases in color intensity but 5 p.p.m. of W does not harm. Copper may not exceed 10 p.p.m. and in its presence the pH must lie between 2.5 and 4.0. Nickel interferes by producing a change in hue and raising the transmittance below 540 mμ, so that no more than 2 p.p.m. may be present. Cobalt gives a yellow color and shoult not exceed 10 p.p.m. at pH 3-5. Sn^{+2} should not exceed 20 p.p.m. for pH 2-3, and Sn^{+4} should not be above 50 p.p.m. (pH 2.5).
>
> If the pH is kept above 6 and 3, respectively, oxalate and tartrate in concentrations as high as 500 p.p.m. do not interfere. In the presence of pyrophosphate the pH must be above 6; then 50 p.p.m. of $P_2O_7^{+4}$ causes an error of only 1 percent with 2 p.p.m. of iron. Phosphate may be present up to 20 p.p.m. of P_2O_5 (pH2-9). Fluoride (500 p.p.m.) does not interfere if the pH is kept above 4.0. Chloride and sulfate are without effect, at least in moderate amounts. If perchlorate is present in more than small amounts, a precipitate of the slightly soluble 1, 10-phenanthroline perchlorate may be produced."

Fortunately, these interfering substances usually are present in such low concentrations in ground waters that their effects generally are not of any significant concern in the normal determination.

The ortho-phenanthroline color complex with iron has been shown to be very stable when employed in the determination of total iron and in the presence of excess ortho-phenanthroline and hydroxylamine-hydrochloride. Under normal laboratory conditions, the stability of color lasts up to six

months or more within the pH range of 2 to 9 (43). In an accelerated fading test using ultraviolet irradiation the color was found to be stable and unchanged after 100 hours (16). However, in the presence of both ferrous and ferric complexes, the color has been found to change with time due to the unstable equilibrium condition of ferrous and ferric iron in the solution. Harvey and his associates (21) performed an experiment using ortho-phenanthroline in two solutions; one contained 10 mg/l of complexed ferric iron and the other 5 mg/l of complexed ferrous iron plus 5 mg/l of complexed ferric iron. They found that there was no appreciable change within 30 minutes. After that time, the change in readings was marked. The increase in absorbance (at 512 mμ) was greater for the mixture than for the ferric iron complex alone. After 15 days, the two solutions had approximately the same absorbance and became stable, from which it was concluded that an equilibrium between the two oxidation states had been reached. Lee and Stumm (31) who performed the ferrous iron determination in the presence of the ferric iron by ortho-phenanthroline also found the color to increase with time. They have explained that the increase in color with time was the resul of the reduction of ferric iron to ferrous iron complex, since ferrous-ortho-phenanthroline complex has a larger stability constant as compared to the ferric-ortho-phenanthroline complex.

It has been found that the orange-red-ferrous-complex color has maximum absorbance at 512 mμ (21) whereas the yellow color complex of ferric iron has its maximum at 360 mμ (20). From this, Harvey and his associates (21) have suggested a rapid method of determining ferrous and ferric iron in a solution by measuring the absorbance at 513 mμ for ferrous iron and 396 mμ for total iron since he found that both ferrous and ferric-ortho-phenanthroine complexes have equal absorbance at 396 mμ. However, the accuracy of this procedure is still questionable. The wavelength of 510 mμ with a

light path of 1 to 10 cm has been recommended in Standard Methods (2) for the determination of both ferrous and total iron by the ortho-phenanthroline method.

The lower limit of sensitivity for iron using ortho-phenanthroline and a photometric measurement is found to be about 0.5 mg/l (46), with a precision and accuracy under optimum conditions, according to Standard Methods (2), of 1 per cent (of absorbance) or 0.001 mg, whichever is the greater. However, the precision and accuracy also will depend on the method of sample collection and storage, and the iron concentration. The variability and instability in sampling will limit the precision and accuracy of this determination more than will the errors inherent in the analysis itself.

The new reagent 4:7 - diphenyl - 1:10 - phenanthroline (batho-phenanthroline) has proved to be more sensitive than ortho-phenanthroline in many respects. Not only is the molar extinction coefficient of the ferrous bathophenanthroline ion (22,400) about twice that of ferrous - ortho-phenanthroline (11,100) but the new reagent can also be extracted from aqueous solutions with certain immiscible solvents, such as isoamyl alcohol and n-hexyl alcohol. Many important advantages are gained from this: (1) the iron in large samples can be easily concentrated into a small volume for measurement; (2) it is easy to free the necessary reagents from iron, which eliminates the blank correction; (3) the ferrous - bathophenanthroline complex is readily extracted by immiscible solvents which would tend to stabilize the developed colors; (4) the extraction procedure renders the method less subject to interferences from ferric iron and other interfering substances.

B. Redox Potentials

1. Principles of Redox Potential Measurement

Chemical reactions are classified into various types as "combination", "direct union", "decomposition" and "oxidation-reduction". As the name

implies, the oxidation-reduction (redox) potential measurement involves an oxidation-reduction reaction.

Oxidation may be defined as a process in which (22):

a. the proportion of oxygen in acid forming elements or radicals is increased;

b. hydrogen is removed; or

c. a loss of electrons occurs with a resulting increase in positive valence; inversely, reduction would involve

   (a) a loss of oxygen;

   (b) a gain of hydrogen; or

   (c) a gain in electrons, reflected by a decrease of positive valence.

For every oxidation reaction, there must be a simultaneous reduction reaction since free electrons cannot accumulate. A substance may be oxidized or reduced. However, another substance must be present to be reduced or oxidized; to either take or give electrons to the first substance.

Although oxidation and reduction always occur together, the process may be written separately as half-reaction equations. For example the oxidation of iodide to iodine by hypochlorous acid (14),

$$HOCl + H^+ + 2I^- = I_2 + Cl^- + H_2O$$

may be separated into two half-equations, one

$$2I^- = I_2 + 2^- \text{.....(a)}$$

representing the oxidation of iodide, and the other

$$HOCl + H^+ + 2e^- = H_2O + Cl^- \text{.....(b)}$$

representing the reduction of the HOCl. Addition of these half equations, neither of which occurs by itself, gives the complete oxidation-reduction equation.

When a metallic electrode is placed in water, it will be dissolved to some extent. In this reaction, metallic ions are considered to pass into solution, and the electrode becomes negatively charged. The extent of the negative charge that accumulates on a metallic electrode is a function of the solution pressure of the metal, hence a potential is developed. This corresponds to the well-known electromotive force series of the metals. When the potentials are measured in terms of a normal hydrogen reference electrode and in a solution containing 1 gm. ionic weight of the metallic ion per 1,000 gm of water, the potentials obtained are called "normal electrode potentials", and they are usually represented by the symbol "Eo" (44). The chart of normal electrode potentials for various metals have already been established and generally can be found in most texts which consider electrochemistry.

Owing to different normal electrode potentials, when a pair of different metallic electrodes both immersed in a salt solution is connected through a conductor, a galvanic cell will result. The electrons will flow from the electrode of higher potential to the electrode of lower potential. This reaction also is classified as an oxidation-reduction reaction. For example, if a pair such as zinc and iron is employed, the reaction of each electrode can be written as follows (26):

Zinc electrode: $Zn^{o} = Zn^{++} + 2e^{-}$ (Oxidation)

Iron electrode: $Fe^{++} + 2e^{-} = Fe^{o}$ (Reduction)

The overall oxidation-reduction reaction is then

$$Zn^{o} + Fe^{++} = Zn^{++} + Fe^{o}$$

There is another type of oxidation-reduction that involves only a change in the charge of the constituent ions. The electrode material needs not participate in the reaction; it may be an inert metal that serves as a source or sink for electrons and as a conductor. It is necessary,

however, that equilibrium conditions for the half-reaction of interest be established at the electrode surface. Potential can thus be determined, at least in theory, for any reaction yielding or utilizing electrons, i.e., for any oxidation-reduction reaction. For example, an inert platinum wire dipping into a solution of ferrous and ferric ions (half reaction $Fe^{++} = Fe^{+++} + e^{-}$), and also through a voltmeter to another system of the standard platinum hydrogen electrode, corresponding to the equilibrium of the half-reaction [H_2 (gas) = $2H^{+} + 2e^{-}$], would result in the oxidation of the ferrous ions (Fe^{++}) to ferric ions (Fe^{+++}) and in the reduction of hydrogen ion (H^{+}) to unionized hydrogen molecule (H_2^{o}). The reaction would be written as follows:

$$Fe^{+2} + H^{+} = Fe^{+3} + 1/2H_2^{o}$$

The potential of the standard hydrogen electrode with the hydrogen ion at unit activity and the hydrogen gas at 1 atmospheric pressure is universally taken as standard and is assigned an electrode potential of zero at each temperature (11).

The magnitude of the oxidation potential of a system, referred to the hydrogen electrode, is expressed by the symbol Eh and is given by the equation derived from the Nernst equation (19, 30).

$$Eh = Eo + \frac{RT}{nF} \ln \frac{[Ox]}{[Red]}$$

$$E_h = E_o + \frac{k}{n} \log \frac{[Ox]}{[Red]}$$

in which

E_h = The measured electrode potential in volts, in reference to the standard hydrogen electrode;

E_o = A standard potential of the system at 30^{o} C. when the activities of all oxidants and reductants are unity.

$$k = \frac{Rt}{2.303\ F}$$

R = 8.315 volt - joules coulombs (the gas constant)

T = The absolute temperatures in degrees Kelvin

F = The faraday constant = 96,500 coulombs

n = The number of electrons that participate in the potential system

[Ox] and [Red] are molal concentrations of oxidant and reductant after correction for activity.

Taking into account the difference between common and Napierian logarithms, ln = 2.3026 log x; the value of the constant

$$k = \frac{Rt}{2.303F} = 0.06011 \text{ at } 30^{\circ}C,\ 0.0592 \text{ at } 25^{\circ}C$$

For example, in the ferrous-ferric system ($Fe^{++} = Fe^{+++} + e^{-} +$ 0.771v) at 25°C the equation becomes:

$$E_h = 0.771 + 0.0592 \log \frac{[Fe^{+3}]}{[Fe^{+2}]}$$

From the general equation of E_h it should be noted that the greater the proportion of reduced substance present, the lower will be the E_h value; conversely, the greater the portion of oxidized substance the higher will be the E_h value. In other words E_h is not really the measure of concentration of the oxidized or the reduced substance, but it is the measure of the ratio of the concentration. For example, the E_h of a system having the concentrations of [Ox] and [Red] of 100 and 10 molals respectively will be theoretically equal to that of a system having [Ox] and [Red] concentrations of 10 and 1 respectively. When the molal concentrations of oxidant and reductant are equal, the term E_h becomes equal to E_o, regardless of concentration (26).

Although standard potentials are normally referred to the hydrogen electrode, some other electrode is usually used as the reference since a potential is experimentally measured as the hydrogen electrode is somewhat inconvenient to use. Electrodes whose potential with reference to the hydrogen electrode are accurately known are normally chosen for their ease of preparation and reproducibility. They usually consist of a system made of a metal, insoluble salt of metal, and a solution containing an ion in common with the salt. The most commonly used reference electrode is the calomel electrode. This electrode is essentially a mercury-mercurous ion electrode, in which the half-cell reaction can be represented as follows (11):

$$Hg_2Cl_2 + 2e^- = 2H_g + 2\ Cl^-$$

Another reference electrode also commonly used is the silver-silver chloride reference half-cell consisting of a silver electrode (Ag) in contact with silver chloride (Ag Cl). The silver and silver ions (Ag, Ag^+) are the reduced and oxidized forms of this reference half cell. The silver-silver chloride electrode has an advantage over the calomel electrode in that it has greater stability at higher temperature (24).

All O.R.P. measurements which employ either a calomel or silver-silver chloride as a reference can be converted to the potential with reference to hydrogen electrode by applying a correction factor. This can be expressed by the following equation (24).

$$E_h = E + \text{voltage of reference electrode}$$

where E_h = The potential with reference to the hydrogen electrode.

E = Observed voltage with calomel or silver-silver chloride.

Potential of standard hydrogen electrode = 0.00 volts

Potential of silver-silver chloride reference = 0.199 volts

Potential of standard hydrogen electrode = 0.244 volts

In practical applications, the conversion factor of the standard calomel is sometime taken as = 0.250 volts.

2. Factors Affecting Redox Potential Measurements

There are a number of conditions affecting the potential as well as the rate of change of potential. Generally, these influential factors are:

1. Oxidants and reductants in the system. All oxidants and reductants present and the tendency of the system to take or give off electrons. For example, it has been theoretically calculated that in a system where the redox potential is solely determine by the oxygen tension, a reduction in oxygen concentration from 10 gm/l to 0.1 mg/l will lower the potential by 30 millivolts (48).
2. The pH of the system. The pH of the solution affects the activity of the ions involved. In addition, through formation of hydroxide, it affects the precipitation of solid hydroxides.

Bass Becking and his associates (6) has presented the relationship of redox potentials (E_h) to pH for the equilibrium condition as:

$$E_h = E_o - 59(a/n)pH \quad \text{millivolts}$$

in which E_o = Standard oxidation potential.

a = The number of protons, and

n = The number of electrons taking part in the reaction.

It can be seen that the gradient of the equilibrium line on an E_h - pH diagram is entirely determined by a/n. They also pointed out the fallacy in assumption which has been widely accepted that the slope is always -59 mv per pH unit by using the following illustrations as examples (6):

Reaction: $$Fe^{+2} + 2H_2S \rightleftharpoons FeS_2 + 4H^+ + 2e^-$$

from which a/n = 2 and E_h = -140 - 118 pH

Reaction: $3Fe^{+2} + 4\,H_2O \rightleftharpoons Fe_2O_4 + 8H^+ + 2e^-$

From which $a/n = 4$ and $E_h = +990 - 237\ pH$

3. The temperature of the system. The temperature of the solution influences the potential but only slightly. The necessary correction will usually be less than 1 millivolt per degree centigrade. This value varies with the electrode being used. However, temperature may exert the indirect effect significantly as it affects the oxidation-reduction reaction rate since, in most processes, reaction rates accelerate with increasing temperature.

In connection with the factors discussed above, the following factors have also been found to not only affect the potential measurement but also limits is applicability and accuracy as well.

1. The surface of the electrode can become desensitized by the effect so called "poisoning of electrode". A surface film of platinum oxides may be formed on the platinum electrodes when the electrodes are immersed in aqueous media which make the voltametric behavior differ dramatically from that of an unoxidize electrode (4, 48).

2. The platinum surface can exhibit a memory effect by exposure to strong oxidant or reductants with subsequent residual influence (24).

3. The length of time allowed for stablized potential measurement. It has been often found that the equilibrium redox potential reading varies with time. It has been suggested that the time allowed for the readings to reach equilibrium should be consistent. For example, assuming that 10 minutes required to reach equilibrium in the initial sample, then all subsequent samples should be given the same time for equilibration.

Only the final stabilized reading (10 minute reading in this case) should be recorded, any and all intermediate figures serving only to show by their increments how dynamic or static the system is.

IV. EXPERIMENTAL EQUIPMENT AND PROCEDURES

A. Analysis of Ferrous Iron

1. Preparation and Collection of Samples

Samples used in determining ferrous iron were either made with distilled water or obtained from natural raw water. For distilled water samples, ferrous ammonium sulfate, $Fe(NH_4)_2SO_4 \cdot 6H_2O$, was used to yield ferrous iron. Since the ferrous iron existing in this compound is very stable, the exact amount of ferrous iron then can be determined. The ferrous ammonium sulfate was weighed out to the closest 0.1 mg by the use of a Sartorious balance. For example, if a solution of 0.10 mg per ml. of ferrous iron was required, 0.7022 gm. of ferrous ammonium sulfate was weighed out. The weighed amount of ferrous ammonium sulfate then was dissolved in 20 ml. of conc. H_2SO_4 and 50 ml. of distilled water.*1 This solution was then diluted with distilled water to 1,000 ml. and mixed well. This solution may be called a "stock solution," and, in general, was prepared such that it would contain 0.1 mg of ferrous iron per 1.00 ml. The more dilute solutions were then prepared from this solution by pipetting varying volumes of the stock solution into a 1-liter volumetric flask and diluting to the mark with distilled water.

For standard ferric iron solution, ferric ammonium sulfate [$Fe(NH_4)(SO_4)_2 \cdot 12H_2O$] was used and the preparation of the solution was similar to that of ferrous ammonium sulfate. For example, if 0.2 mg. of ferric iron per 1.00 ml. was required, 1.7268 gm. of ferric ammonium sulfate would be dissolved in 20 ml. conc. H_2SO_4 and 50 ml. distilled water then diluted to a liter.

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*1 All distilled water referred to here after is understood as "Iron-free distilled water."

For the distilled water iron solutions containing a mixture of ferrous-ferric iron, the ferrous ammonium sulfate and ferric ammonium sulfate solutions which had been prepared as above were used by pipetting proportional amounts of the standard solutions into 1-liter volumetric flask accordingly and diluting with distilled water to the mark.

For example, if solution of 0.002 mg. ferrous - 0.002 mg. ferric iron per 1.00 ml. of sample was required, the solution was prepared by pipetting 20 ml. of the 0.1 mg-ferrous per 1.00 ml. standard ferrous solution and 10 ml. of the 0.1 mg-ferric per 1.00 ml. standard ferric solution into 1-liter volumetric flask. The mixture then was diluted to mark with distilled water and mixed. This solution then contained 0.002 mg. ferrous and 0.002 mg. ferric iron per 1.00 ml.

Natural raw ground waters from various wells in Illinois were used as the natural sources of ferrous iron. Water samples were collected in the field, using precautions not to aerate the water, and transported to the laboratory in 18 gallon glass bottles. Since no constant temperature bath was available in transporting the water samples to the laboratory, a few degree rise in water temperature sometimes was observed. If the experiment could not be performed on the same day on which the samples were collected, the samples were stored over night in a refrigerator at about 10°C.

2. Method of Analysis

Two methods for analysis of ferrous iron were used in this study: (1) the bathophenanthroline method which employed 4,7-diplenyl - 1, 10 phenanthroline ($C_{24} H_{16} N_2$).*2 The procedure used was essentially that described by Lee and Stumm (31) and (2) the ortho-phenanthroine method using 1, 10 phenanthroline monohydrate ($C_{12} H_8 N_2 \cdot H_2O$).*2

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*2 Both ortho-phenanthroline and bathophenanthroline compounds were the products of the G. Frederich Smith Chemical Co., Columbus, Ohio.

a. Reagents for bathophenanthroline method:

1. Bathophenanthroline, 0.001 M. solutions. It was prepared by dissolving 0.0332 gm of bathophenanthroline in 50 ml of 95 percent ethyl alcohol and diluting to 100 ml. with distilled water.

2. Hydroxylamine hydrochloride, 10 percent solution. The solution was prepared by dissolving 10 gm of hydroxylamine hydrochloride in 100 ml. of distilled water and stored in a glass stopper reagent bottle.

3. Sodium acetate, 10 percent solution. The solution was prepared by dissolving 10 gm. of sodium acetate in 100 ml of distilled water.

4. Extracting alcohol. Reagent grade isoamyl alcohol was used.

5. Ethyl alcohol, 95 percent, reagent grade.

6. Standard iron solution. The standard iron solutions for ferrous and ferric iron were prepared from ferrous ammonium sulfate and ferric ammonium sulfate as previously described. The standard iron wire solution was also used as a reference. The standard iron wire solution was prepared by weighing out 0.2000 gm. of the well-polished "iron wire for standardizing" and dissolved in 20 ml. 6N . H_2SO_4 and diluted to the mark with distilled water. This stock solution then contained 0.20 mg iron per 1.00 ml. The more dilute solutions were then prepared from this stock solution by diluting with distilled water accordingly.

b. Procedure for determining iron by bathophenanthroline:

The sample (water being tested or standard iron solution) was pipetted into a 125 ml. separatory funnel. The usual volume used was 10 ml; however, for very high concentration of iron, only 5 ml was used. A reagent blank consisting of 10 ml of distilled water was also prepared. To each sample 4 ml. of the 10 percent sodium acetate solution was added. The pH of the solutions at this point were tested and found to be about 4. An additional 4 ml of sodium acetate solution was used where the original sample

of water had been acidified. Two ml. of hydroxylamine hydrochloride were added to each sample if the sample was being tested for total iron. The hydroxylamine was omitted when the ferrous iron concentration was sought. 15 ml of 0.001 M. bathophenanthroline solution was then added, mixed, and followed by 10 ml. of isoamyl alcohol. This mixture was shaken thoroughly. The liquids then were allowed to separate for at least 5 minutes after shaking. After the liquids had cleanly separated into two layers, the lower aqueous layer was drawn off and discarded. This isoamyl alcohol layer was drained into a 50 ml volumetric flask and the separatory funnel was then washed with about 5 ml of ethyl alcohol added from a pipette. This was done in such a manner that the upper stopper of the funnel and the walls of the funnel were uniformly washed at least twice by a film of alcohol as it drained from the top to the bottom into the volumetric flask. The solution was then diluted to the 50 ml. mark with ethyl alcohol and mixed by shaking. The intensity of the color was then measured and expressed as percent transmittance by using a spectrophotometer*3 at a wavelength of 533 mμ with a slit opening of 0.002 mm. and a light path of 1.0 cm. From the values of percent transmittance obtained, the amount of iron present then can be calculated from the standard curve.

The standard calibration curve was established by the use of the standard iron wire solution and the standard ferrous ammonium sulfate solution using about 10 different concentrations. The iron-bathophenanthroline color conforms to Beer's law, so that the plot of percent transmittance and concentration of iron on semi-logarithmic paper yielded a straight line.

The ortho-phenanthrlline method employed was essentially that as given in the 10th and 11th Ediction of Standard Methods (2, 3), with some modifications.

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*3 Model DU, made by Beckman Instruments, Fullerton, California.

a. Reagents for orthophenanthroline method:

1. Hydrochloric acid, conc.

2. Hydroxylamine reagent. The solution was prepared by dissolving 10 gm. NH_2OH . HCl in 100 ml. of distilled water.

3. Ammonium acetate buffer solution. 250 gm. of ammonium acetate (CH_3COONH_4) were dissolved in 150 ml. distilled water, 700 ml. glacial acetic acid were added and the solution then was diluted to 1 liter with distilled water.

4. Sodium acetate buffer solution. The solution was prepared by dissolving 350 gm of sodium acetate (CH_3COONa) in 500 ml. distilled water and dilute to approximately 1 liter. The sodium acetate solution then was adjusted with distilled water such that 10.0 ml. of the solution when added to 2.0 ml. HCl and 100 ml. distilled water, would yield the pH to a value between 3.2 and 3.3.

5. Ortho-phenanthroline solution. 1 gm. of 1, 10-phenanthroline monohydrate ($C_{12}H_8N_2 . H_2O$) was dissolved in 1,000 ml. of approximately 80°C distilled water. The solution was kept away from the light in the dark brown bottle.

6. Standard iron solution. For the calibration of a standard ferrous iron curve, the solutions were prepared from the freshly made standard ferrous ammonium sulfate stock solution. Both ferrous ammonium sulfate and "iron wire for standardizing" stock solutions were used in the calibration of the standard total iron curve.

b. Procedure of determining ferrous iron by ortho-phenanthroline:

Many modified methods for determining ferrous iron by the use of ortho-phenanthroline were investigated and included;

1. "Ortho-phenanthroline only": 10 ml. of the ortho-phenanthroline solution was placed in 100 ml. volumetric flask. The sample (water

being tested or standard iron solution) was pipetted into the flask and the solution diluted to the mark. The fixed sample then was filtered through fine (Whatman No. 40) filter paper or 0.45μ membrane filter*4.

2. "Ortho-phenanthroline plus sodium acetate and HCl": 2 ml. of conc. HCl were placed in a 100 ml. volumetric flask, and the sample being tested for iron was pipetted into the flask. 10 ml. of sodium acetate buffer solution and 10 ml. of ortho-phenanthroline solution were then added and the solution was diluted to the mark with distilled water.

3. "Ortho-phenanthroline plus sodium acetate": 10 ml. of sodium acetate buffer and 10 ml. of ortho-phenanthroline were placed in a 100 ml. volumetric flask, the sample being tested were pipetted into the flask and diluted to the mark with distilled water.

4. "Ortho-phenanthroline plus ammonium acetate": 10 ml. of ammonium acetate buffer and 10 ml. volumetric flask, the sample being tested was then pipetted into the flask and the mixture was diluted to the mark with distilled water.

5. "Acidified samples": Where the samples being tested had been acidified with hydrochloric or sulfuric acid to pH 1.0, the method as described under 4. (ortho-phenanthroline plus ammonium acetate) was used.

The colorimetric measurements for the methods described above usually were made against a pure distilled water blank. However, in some cases, the color and turbidity due to iron flocs were quite apparent, each reading then was made against a "adjusted blank" in the case of both color and turbidity interferences, and against an "acidified adjusted blank" in the case of only the color interference. The "adjusted blank" was made up by using proportional volume of a sample added to distilled water. When

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*4 Cellulose nitrate membrane filter used in this study was manufactured by Millipore Filter Co.

the turbidity changed with samples, many "adjusted blanks" were prepared correspondingly for each sample. The "acidified adjusted blank" was prepared similarly to the "adjusted blank" but with a few drops of hydrochloric acid added.

c. Procedure for determining total iron by ortho-phenanthroline:

The procedure for determining total iron by ortho-phenanthroline was essentially identical to that described in the 11th Edition of Standard Methods (2). The sample was mixed thoroughly and 50 ml. (or smaller size if the iron concentration was high) were measured into a 125 ml. erlenmeyer flask, 2 ml. for conc. HCl and 1 ml for hydroxylamine reagent were added with a few glass beads and the mixture then was heated to boiling. The sample was allowed to boil for about 5 minutes and was cooled to room temperatures. The solution was transferred to a 100 ml. volumetric flask, 10 ml. ammonium acetate buffer solution and 10 ml. ortho-phenanthroline solution were added and the mixture was diluted to the 100 ml. mark with distilled water. The colorimetric measurement then was made against a pure distilled water blank.

The intensity of color of both ferrous and total iron samples was measured as percent transmittance. The standard calibration curve for ferrous iron was established by the use of standard ferrous ammonium sulfate solution, while both standard iron wire and ferrous ammonium sulfate solutions were used for the total iron standard curve.

B. Redox Potential Measurement

1. Apparatus

The redox potential of the water was measured with the use of a flow cell as shown in Fig. 2. The cylindrical cell was made of "Lucite", and had a diameter of approximately 4 inches, and was 5 inches in height. The flow cell was closed at the bottom with a large rubber plug. The top of

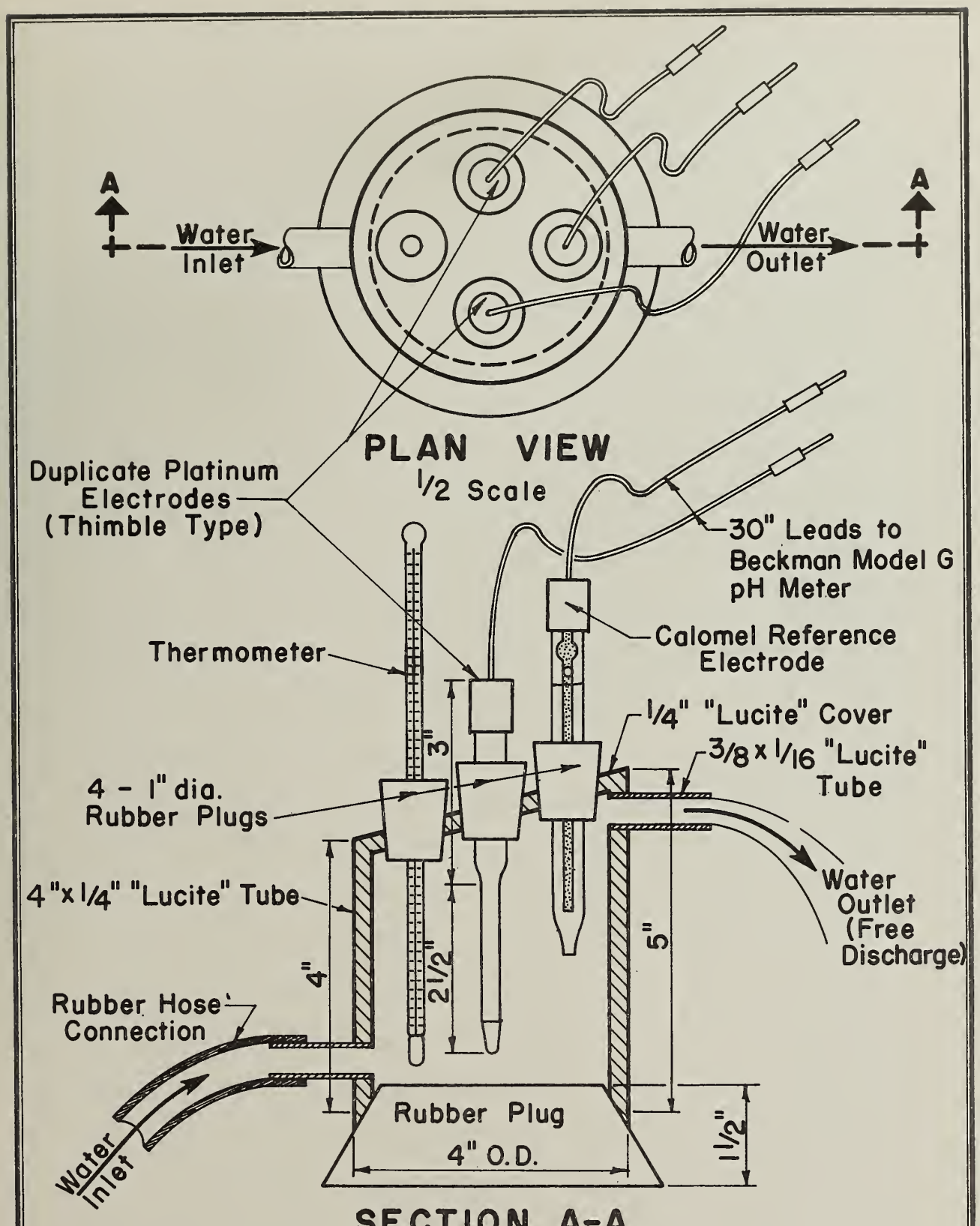

FIGURE 2

FLOW CELL DEVICE

the flow cell was covered with a Lucite plate cemented to the cylindrical body at an angle of about 45° as to facilitate the release of gas bubbles. The four openings at the top of the flow cell were stoppered with No. 5 rubber plugs, through which the thermometer and three electrodes were inserted into the cell. The thermometer was inserted through the hole at the lowest level while the calomel reference electrode was located at the highest level. The two mid-level holes were used for two duplicate platinum electrodes. The water was allowed to enter the flow cell through the inlet which was close to the bottom of the cell and was freely discharged through the outlet close to the top at a rate of about 0.5 to 1 gallon per minutes. The electrodes used in redox potential measurement consisted of two thimble type platinum electrodes*5 and one fiber type calomel electrode.*6. The meter used for measuring redox potentials was a Model G pH meter manufactured by Beckman Instruments, Inc. The pH of water was measured separately in a beaker by a Beckman Instruments, Inc. Model N pH meter.

2. Procedure for Measuring Redox Potentials.

After the flow cell had been arranged as shown in Fig. 2, the electrodes were connected to the meter and the water was allowed to enter the cell. The first reading was made at approximately 5 minutes after connection, when the needle of the meter became stable. Another reading was taken at about 5 minutes after the first reading. The first platinum electrode then was disconnected, and was replaced with the second platinum electrode, and one reading again was made at about 5 minutes and another at 10 minutes after connection. All of the four readings taken with these two platinum electrodes should agree within 20 mv. It was found that the readings which were taken at the end of 10 minutes did agree within 20 mv.

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*5 Platinum electrode (thimble type) catalog part No. 39271, Beckman Instrument, Inc.

*6 Calomel electrode (fiber type) catalog part No. 39970, Beckman Instrument, Inc.

The reading was then recorded to the nearest 10 mv. If the readings did not give satisfactory agreement, both metal electrodes then were removed from the flow cell and the platinum surfaces soaked in conc. sulfuric acid for about 30 seconds, rinsed with distilled water, and thoroughly wiped with a soft tissue paper. Both electrodes then were inserted back into the flow cell and the whole process of measurement was repeated. After cleaning, the readings were usually improved and agreed quite well. The acidified redox potential measurements were made by lowering the pH of the water samples to pH 1.0 with conc. sulfuric acid, and the redox potential readings were obtained quite rapidly within 1-2 minutes since equilibrium was reached in a much shorter time than that of the natural raw water.

The redox potential measurement and other chemical analysis were made at various stages of the unit treatment process, which included raw, after aeration and "after filtration" or finished stages. At each stage two ferrous iron samples (one at the beginning and one at the end of redox potential measurement), one total iron sample and one dissolved oxygen sample were taken. Usually 25 or 50 ml. of samples were used for ferrous iron determination and was added directly to a 100 ml. volumetric flask which contained 10 ml. of ortho-phenanthroline solution only. The mixture was then diluted to the mark and filtered through fine (Whatman No. 40) filter paper. The dissolved oxygen determination was done in the field by the use of the Azide Modification of the Winkler Method as described in the 11th Edition of Standard Methods (2). Nitrate determinations were made in the field with the use of a test developed by Bray (8) known as "Nitrate Tests for Soils and Plant Tissues." The reagent consists of a mixture of powdered zine and dry citric acid, which are to reduce the nitrate to nitrite, and a standard indicator which produces pink color with nitrite. The color indicated can give the rough estimation of the nitrate existed.

The ranges of nitrate are divided into four classes according to the color prevailed, "high" for which the pink color appearance was very bright, "medium" for moderate pink, "slight" for slight pink and nil for those which gave no pink color at all. The degree of increase in nitrate was obtained from the comparative values as described above. If the increase was from nil to medium or from slight to high, the increase in nitrate content would be reported as "large increase". The water temperature was also recorded. About one gallon of water at each stage was brought back to the laboratory for additional analysis which included total solids, total and calcium hardness, chloride and chemical oxygen demand. The methods of determinations in the laboratory follow those set forth in the 11th Edition of Standard Methods (2).

Total Solids.	Residue on Evaporation
Total Hardness.	E D T A Titration Method (Univer II[*7] as indicator)
Calcium Hardness.	E D T A Titration Method (Calver 11[*7] as indicator)
Chloride.	Mercuric Nitrate Method
Chemical Oxygen Demand.	Dichromate Reflux Method (0.025 N Standard potassium dichromate was used, silver sulfate was added at 1 hr. after refluxing for complete chloride correction)

*7 Both Univer-II and Calver--11 compounds were the products of the Hach Chemical Company, Ames, Iowa.

V. EXPERIMENTAL RESULTS

A. Analysis of Ferrous Iron

Table 1 shows the results of determining iron by modified methods of ortho-phenanthroline and bathophenanthroline using distilled water samples containing ferrous and ferric iron. Unless otherwise specified, the ortho-phenanthroline samples were compared with a distilled water blank, while the bathophenanthroline was read against a distilled water-reagent blank. The methods used are indicated at the end of the Table. Samples with varying ratios of ferrous to ferric iron were set up in order to determine and compare the accuracy of various methods of determining ferrous iron in the presence of ferric iron. The calculated amounts of ferrous and ferric iron were obtained by computation from the equivalent weight of ferrous and ferric ammonium sulfate standard solutions, respectively. Total iron is the sum of both the ferrous and ferric iron in the samples. The results in Table 1 are expressed in milligrams (mg), in terms of the amount present in the volume used for color development.

The values of ferrous iron obtained using ortho-phenanthroline with the buffers, sodium acetate and ammonium acetate, or with the buffer plus hydrochloric acid are consistently higher than the calculated values, especially where samples have a low ratio of ferrous to ferric iron. The method which employed ortho-phenanthroline only was found to give results close to the calculated values and to those obtained by the bathophenanthroline method. However, when only ferrous iron was present, the results of all three methods were in generaly lower than the calculated values, but comparable to one another.

Table 1

RESULTS OF FERROUS IRON DETERMINATION IN SYNTHETIC FERROUS - FERRIC IRON SAMPLES

Ratio Fe^{+2} : Fe^{+3}	Ferrous Iron, mg						Total Iron, mg		
	Calc.	1	2	3	4	B	Calc.	TO	TB
1:4	0.010	0.017	0.018	0.017	0.021	-	0.050	0.065	-
1:4	0.010	0.014	-	-	0.014	0.011	-	-	-
1:4	0.020	0.027	0.031	0.029	0.033	-	0.100	0.109	-
1:4	0.020	0.021	-	-	0.024	0.022	-	-	-
1:4	0.030	0.030	-	-	0.035	0.032	-	-	-
1:4	0.040	0.040	-	-	0.048	-	-	-	-
1:4	0.050	0.057	0.059	0.061	0.061	-	0.250	0.259	-
1:4	0.100	0.100	0.101	0.111	0.118	-	0.500	0.500	-
1:1	0.025	0.026	0.030	0.023	0.023	-	0.050	0.050	-
1:1	0.025	0.036	-	-	0.034	0.026	-	-	-
1:1	0.050	0.050	0.053	0.050	0.056	-	0.100	0.100	-
1:1	0.050	0.050	-	-	0.058	0.052	0.100	0.100	0.103
1:1	0.075	0.078	-	-	0.079	0.077	-	-	-
1:1	0.125	0.122	0.128	0.125	0.131	-	0.250	0.250	-
1:1	0.125	0.125	-	-	0.134	0.129	-	-	-
1:1	0.250	0.251	0.253	0.255	0.255	-	0.500	0.500	-
4:1	0.040	0.049	0.048	0.044	0.044	-	0.050	0.054	-
4:1	0.040	0.040	-	-	0.042	0.042	-	-	-
4:1	0.080	0.085	0.082	0.083	0.086	-	0.100	0.104	-
4:1	0.080	0.078	-	-	0.080	0.083	-	-	-
4:1	0.120	0.116	-	-	0.120	0.125	-	-	-
4:1	0.160	0.157	-	-	0.161	-	-	-	-
4:1	0.200	0.197	0.197	0.207	0.212	-	0.250	0.256	-
4:1	0.400	0.364	0.366	0.408	0.408	-	0.500	0.500	-

Table 1 (Continued)

RESULTS OF FERROUS IRON DETERMINATION IN SYNTHETIC FERROUS - FERRIC IRON SAMPLES

Ratio Fe^{+2} : Fe^{+3}	Ferrous Iron, mg						Total Iron, mg		
	Calc.	1	2	3	4	B	Calc.	TO	TB
1:0	0.050	0.047	-	0.049	0.049	-	0.050	0.049	-
1:0	0.125	0.122	-	0.122	0.123	-	0.125	0.123	-
1:0	0.250	0.248	-	0.255	0.250	-	-	-	-

Ferrous Iron:

1: ortho-phenanthroline only
2: ortho-phenanthroline plus sodium acetate and HCl
3: ortho-phenanthroline plus sodium acetate
4: ortho-phenanthroline plus ammonium acetate
B: bathophenanthroline

Total Iron:

Calc: calculated value
TO : ortho-phenanthroline for total iron (11th Ed. Standard Methods)
TB : bathophenanthroline for total iron

The results of determining ferrous iron in natural waters by the three modified ortho-phenanthroline methods and the bathophenanthroline method are shown in Table 2.

Five different water samples were collected at the Northern Illinois Water Corporation plant which serves Champaign and Urbana, Illinois. Samples were obtained from the inlet main (which is referred to as raw water), during aeration, from the a reaction well, from the top of a filter after the water had been chlorinated, and from the filter effluent (finished water). From Table 2, it appears that the results using the "ortho-phenanthroline only" method of determining ferrous iron are in good agreement with those obtained by the bathophenanthroline method which is regarded as the reference method. The results for total iron as determined by both the ortho-phenanthroline (11th Ed. Standard Method) and the bathophenanthroline show good agreement.

Raw water from the Champaign-Urbana treatment plant (well Number 3) was brought to the laboratory and aerated. Ferrous iron determinations were made on samples taken at various time intervals following aeration. The results of these analyses are given in Table 3 along with a brief explanation of the various analytical methods at the end of the table. It can be seen that the results of determining iron by the acidified sample method give the highest values. The "ortho-phenanthroline plus ammonium acetate" method shows slightly lower values while the results obtained by the "ortho-phenanthroline only" method give the lowest values and show good agreement when compared to the bathophenanthroline method.

Table 4 shows the results of ferrous iron determinations using aerated water treated in a similar manner but obtained from an abandoned well at Cisco, Illinois. In this case the concentration of ferrous iron in raw

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Urbana, Illinois 61801

Table 2

RESULTS OF FERROUS IRON DETERMINATION AT CHAMPAIGN-URBANA, ILLINOIS WATER TREATMENT PLANT

No	Stage	Ferrous Iron, mg/l				Total Iron, mg/l	
		1	2	3	B	TB	TO
1	Raw	0.76	0.80	0.92	0.70	1.00	1.06
2	During Aeration	0.68	0.72	0.88	0.60	1.00	1.06
3	In reaction Well	0.22	0.24	0.28	-	1.00	1.06
4	Top of Filter (Chlorinated)	0.08	0.14	0.18	nil.	1.00	1.00
5	Filter Effluent (Chlorinated)	0.02	0.04	0.08	nil.	0.08	0.10

Ferrous Iron:

1: ortho-phenanthroline only
2: ortho-phenanthroline plus ammonium acetate
3: ortho-phananthroline plus ammonium acetate and HCl
B: bathophenanthroline

Total Iron:

TB: bathophenanthroline for total iron
TO: ortho-phenanthroline for total iron (11th Ed. Standard Methods)

Table 3

RESULTS OF FERROUS IRON DETERMINATION IN AERATED CHAMPAIGN-URBANA, ILLINOIS, GROUND WATER

No	Time after Aeration, min.	Ferrous Iron, mg/l 1	2	3	4	B	Total Iron, mg/l
1	Before Aeration	1.82	2.0	2.20	2.34	1.85	2.38
2	0	1.54	1.86	2.10	2.25	1.27	2.33
3	5	1.30	1.50	2.14	1.90	-	-
4	15	0.64	1.16	1.48	1.60	0.85	-
5	20	0.62	1.08	1.30	1.32	-	-
6	30	0.40	0.80	1.00	1.08	0.49	2.30
7	45	0.19	0.52	0.78	0.74	-	-
8	60	-	0.34	0.54	0.64	0.20	2.38

Ferrous Iron:

1: ortho-phenanthroline only
2: ortho-phenanthroline plus ammonium acetate
3: method same as 2 but samples had been acidified to pH 1.0 with H_2SO_4
4: method same as 2 but samples had been acidified to pH 1.0 with HCl
B: bathophenanthroline

Total Iron: ortho-phenanthroline for total iron (11th Ed. Standard Methods)

Table 4

RESULTS OF FERROUS IRON DETERMINATION IN AERATED CISCO, ILLINOIS, GROUND WATER

No	Time after Aeration, min.	Ferrous Iron, mg/l 1	2	3	4	5	B
1	Before Aeration	12.05	11.75	12.68	12.60	12.50	9.4
2	0	11.52	10.65	12.16	12.30	12.10	8.70
3	10	10.64	9.36	11.48	11.80	11.70	-
4	20	9.76	8.80	10.4	11.1	11.1	6.30
5	30	8.84	7.40	9.60	10.20	9.7	-
6	45	8.00	6.36	8.52	8.90	9.15	4.10
7	75	7.52	4.40	7.16	6.95	6.95	-
8	105	5.62	2.68	5.88	6.92	6.80	-
9	200	3.92	2.16	4.14	3.68	3.60	2.18
Fixed Sample pH		6.9	6.9	3.9	3.9	3.9	-

Ferrous Iron:

1: "ortho-phenanthroline only" method with acidified adjusted blank
2: "ortho-phenanthroline only" method with adjusted blank
3: ortho-phenanthroline plus ammonium acetate
4: method same as 3 but samples had been acidified to pH 1.0 with H_2SO_4
5: method same as 3 but samples had been acidified to pH 1.0 with HCl
B: bathophenanthroline

water was unusually high, and some natural color was present. For those samples which were analyzed by the "ortho-phenanthroline only" method, both color and turbidity interferences were quite apparent. An "adjusted blank", which consisted of a proportional volume of raw water added to distilled water, was used to replace the distilled water blank in the colorimetric measurement in an attempt to compensate for the interferences due to the color and turbidity of the samples. In the methods where the samples were acidified or buffered, the interference due to the turbidity was eliminated since the source of the turbidity, the iron floc, was dissolved at the low pH. The "acidified adjusted blank" was prepared similarly to the "adjusted blank" but with a few drops of acid added so as to eliminate the turbidity. The pH of the solutions after being fixed with ortho-phenanthroline was measured and found to be 6.9 for the "ortho-phenanthroline only" method and 3.9 for both of the "acidified sample" methods and the "ortho-phenanthroline plus ammonium acetate" method. The results of determining ferrous iron by the bathophenanthroline method appear to be quite low as compared to the other methods and some experimental error was suspected because of the delay in completing the determination.

The results shown in Table 5 seem to confirm the previous results in that the "ortho-phenanthroline only" method gives lower values than those obtained by the "ortho-phenanthroline plus ammonium acetate" method and values closer to those found with the bathophenanthroline method. Since it was noted that the time of color development was a critical factor in the determination, the methods were improved by allowing a minimum time of about 10 minutes to elapse between the time the samples were fixed and the time the color measurement was made. The "adjusted blanks" were made up separately corresponding to each sample collected since turbidity was observed to increase with time.

Table 5

RESULTS OF FERROUS IRON DETERMINATION AT INTERVALS IN AERATED CISCO, ILLINOIS, GROUND WATER

No	Time after Aeration min.	Ferrous Iron, mg/l 1	2	B	Total Iron, mg/l TO
1	Before aeration	11.3	11.1	9.0	11.9
2	0	9.3	10.6	8.2	11.8
3	15	8.3	8.80	7.68	-
4	30	7.6	-	6.80	11.5
5	45	5.2	7.60	5.66	-
6	60	4.7	6.80	4.46	11.9
7	75	4.1	5.70	-	-
8	90	3.85	4.90	3.30	-
9	105	2.54	4.63	-	-
10	120	2.44	3.24	-	11.9

Ferrous Iron:

1: "ortho-phenanthroline only" read against adjusted blanks within 10 min.
2: "ortho-phenanthroline plus ammonium acetate" read within 10 min.
B: "bathophenanthroline" read within 10 min.

Total Iron:

TO: ortho-phenanthroline for total iron (11th Ed. Standard Methods)

Table 6 shows the values obtained for ferrous iron using various modifications of the "ortho-phenanthroline only" method and compared with the bathophenanthroline method. Samples, after being fixed with ortho-phenanthroline, were filtered through membrane filters to remove the turbidity. The colorimetric measurements were made immediately after filtration. For methods 2 and 3, the fixed samples were read against corresponding adjusted blanks within 10 minutes, and again after about 30 minutes. The values obtained after filtration and those obtained with the "adjusted blank" using a 10 minute time for color development agree quite well with the bathophenanthroline method. The "adjusted blank" method using a 30 minute period for color development gave generally higher values.

The effect of filtration on color development was determined using the "ortho-phenanthroline only" method and distilled water ferrous iron samples. Five sets of duplicate samples with varying ferrous iron concentrations gave per cent transmittance values within the range of accuracy included in Table 7. The colorimetric measurements were made prior to and after filtration. It can be seen that filtration reduced the intensity of the color slightly and as a result, produced slightly lower values.

Table 8 indicates the instability of the ortho-phenanthroline complex with prolonged periods for color development using aerated Cisco, Illinois water samples. Both the "ortho-phenanthroline only" and the "ortho-phenanthroline plus ammonium acetate" methods were employed by using both methods to determine the ferrous iron remaining at various time intervals after aeration. The results presented in Fig. 4 were obtained from the same experiment as those shown in Fig. 3. The results of ferrous iron determinations, however, were made by the "ortho-phenanthronline only" method with the fixed samples being read against adjusted blank in Fig. 3 and being

Table 6

RESULTS OF FERROUS IRON DETERMINATION AT INTERVALS

IN AERATED DELAND, ILLINOIS GROUND WATER

No	Time after Aeration, min.	Ferrous Iron, mg/l				Total Iron, mg/l
		1	2	3	B	TO
1	Before Aeration	3.16	3.28	3.40	3.36	4.8
2	0	3.48	3.32	3.44	3.36	4.4
3	15	2.96	2.80	3.04	2.87	-
4	30	2.46	2.22	2.46	2.30	4.8
5	45	2.0	1.32	1.92	1.96	-
6	60	1.60	1.52	1.60	1.50	-
7	75	1.08	1.13	1.23	1.10	4.4
8	90	0.87	0.87	0.99	0.90	-
9	105	0.64	0.73	0.72	0.62	-
10	120	0.47	0.51	0.53	0.50	4.4

Ferrous Iron:

1: "ortho-phenanthroline only" and filter immediately through membrane filters
2: "ortho-phenanthroline only" unfiltered, read versus corresponding adjusted blank within 10 min.
3: "ortho-phenanthroline only" unfiltered, read versus corresponding adjusted blank at about 30 min.
B: bathophenanthroline

Total Iron:

TO: ortho-phenanthroline for total Iron (11th Ed. Standard Methods)

Table 7

EFFECTS OF FILTRATION ON ORTHO-PHENANTHROLINE COLOR DEVELOPMENT WITH FERROUS IRON

No	Calc. Ferrous Iron - mg	No Filtration % Transmittance	No Filtration Ferrous Iron, mg	With Filtration % Transmittance	With Filtration Ferrous Iron mg
1	0.010	95.3	0.095	94.6	0.0105
		95.3	0.0095	94.8	0.0105
2	0.020	90.6	0.0210	90.6	0.0210
		90.8	0.0200	91.2	0.0198
3	0.050	79.2	0.0500	79.8	0.0490
		79.4	0.0495	79.7	0.0490
4	0.100	63.1	0.1000	63.8	0.0985
		62.8	0.1150	63.6	0.0995
5	0.200	39.9	0.2250	40.6	0.1995
		39.9	0.2250	40.6	0.1995

Note:

The experimental results of ferrous iron presented is calibrated from the standard curve to the nearest of 0.0005 mg.

Table 8

EFFECT OF TIME ON ORTHO-PHENANTHROLINE COLOR DEVELOPMENT IN AERATED CISCO, ILLINOIS, WATER SAMPLES

Ferrous Iron Present (mg/l)								Total Iron
1-a	1-b		1-c		2-a	2-b		
mg/l	mg/l	% change	mg/l	% change	mg/l	mg/l	% change	mg/l
10.6	10.3	-3	10.4	-2	11.1	11.7	5	11.9
8.80	8.49	4	10.3	18	10.6	11.5	9	11.8
7.80	8.15	5	10.3	32	8.80	11.3	28	-
7.10	8.50	20	9.05	27	-	10.1	-	11.5
4.88	6.65	36	8.70	78	7.60	10.1	33	-
4.10	6.05	47	7.65	86	6.80	9.3	37	11.9
3.83	5.55	45	6.95	79	5.70	8.9	51	-
3.62	4.85	34	6.15	70	4.90	8.1	65	-
2.39	4.60	97	4.98	108	4.63	7.7	66	-
2.30	4.20	83	4.10	78	3.24	7.2	122	11.9

Ferrous Iron:

1-a: "ortho-phenanthroline only" read versus adjusted blank within 10 min. after being fixed.

1-b: "ortho-phenanthroline only" and read versus adjusted blank after 18 hrs.

1-c: "ortho-phenanthroline only" filtered after 18 hrs, then read versus distilled water blank.

2-a: "ortho-phenanthroline plus ammonium acetate", readings were taken within 30 min. after being fixed.

2-b: same as 2-a but readings were taken after 18 hours.

Total Iron: ortho-phenanthroline (11th Ed. Standard Methods)

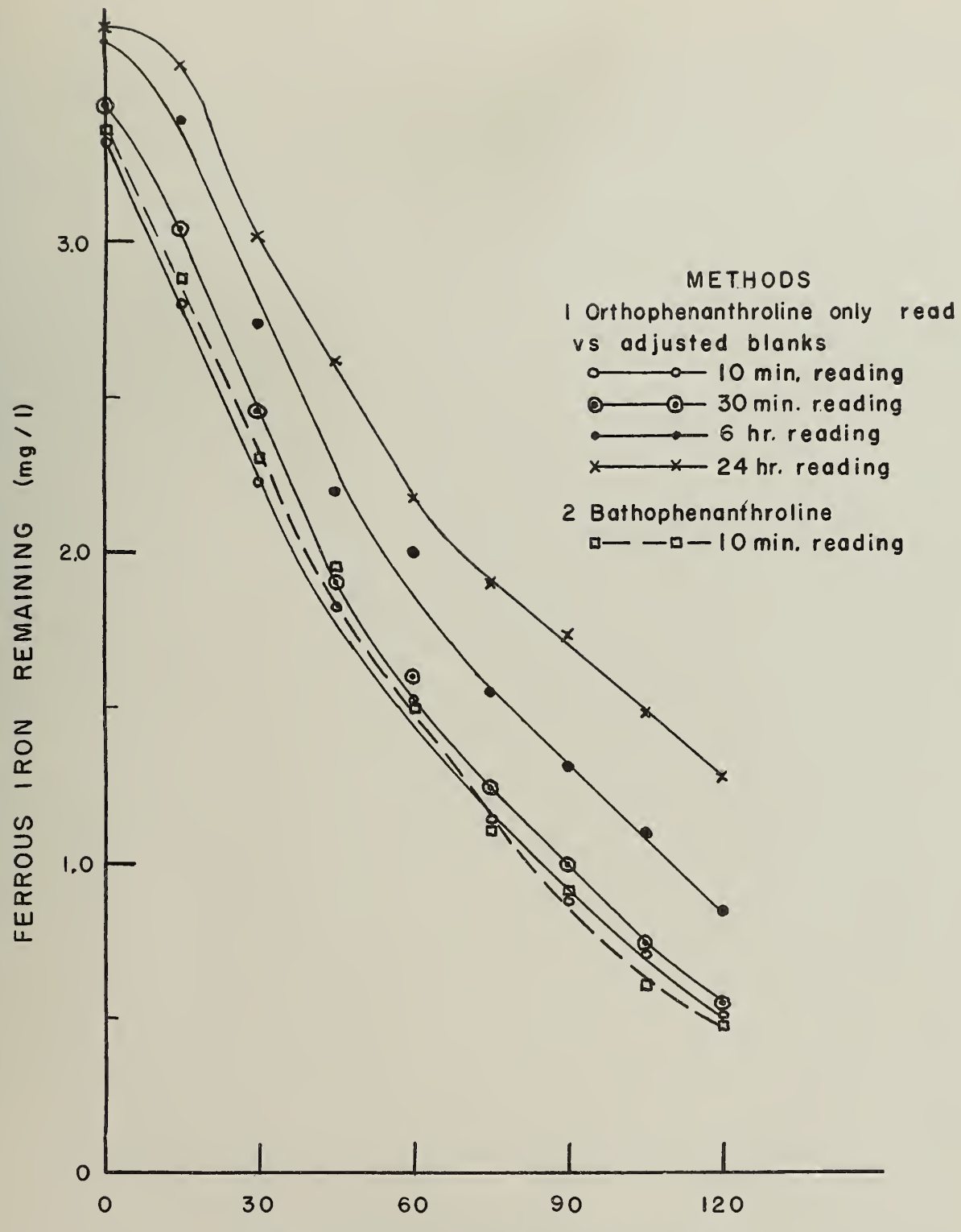

FIGURE 3

RELATIONSHIP OF FERROUS IRON REMAINING TO TIME IN AERATED DELAND GROUND WATER BY "ORTHOPHENANTHROLINE ONLY"- READ VS ADJUSTED BLANKS

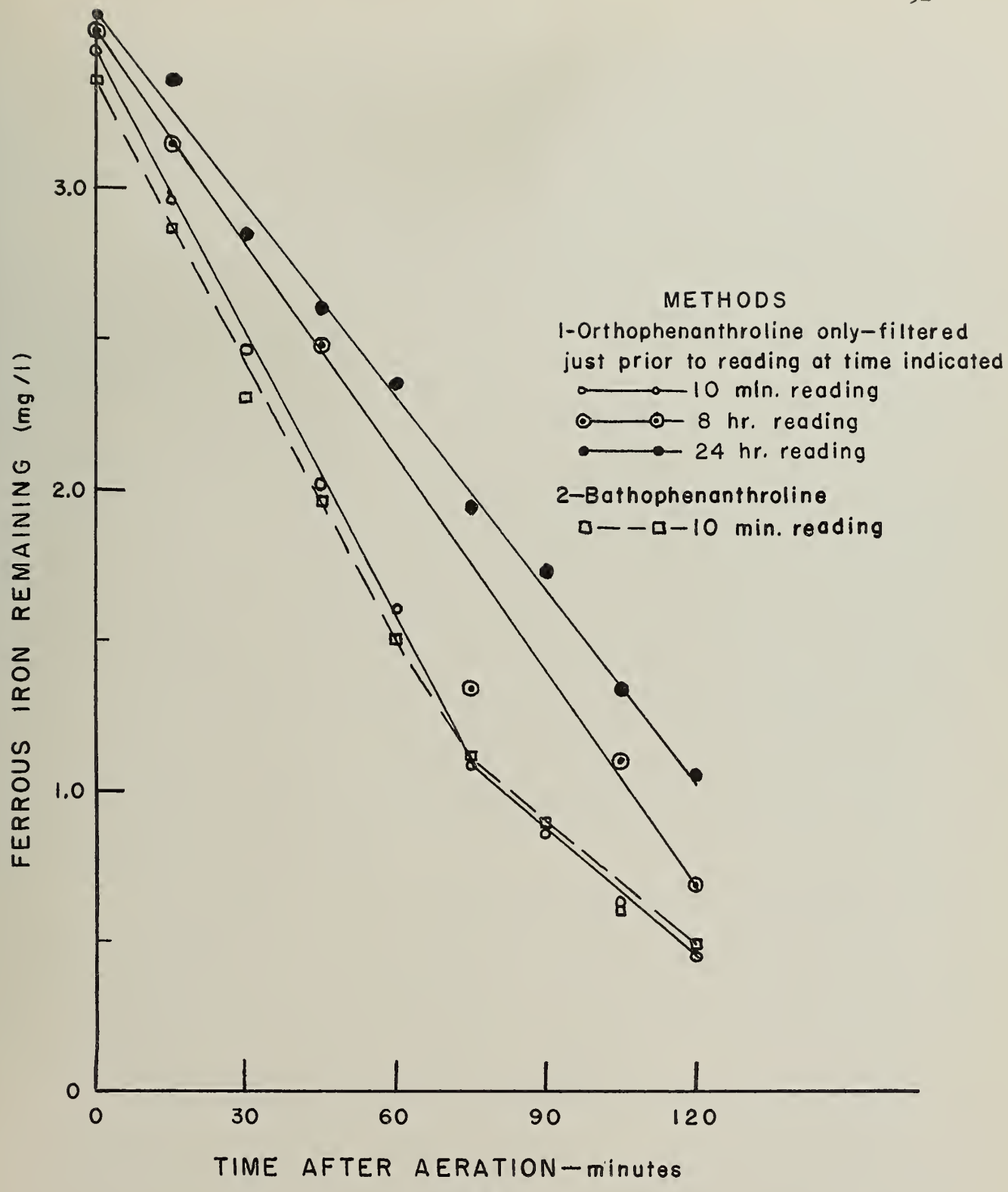

FIGURE 4

RELATIONSHIP OF FERROUS IRON REMAINING WITH TIME IN AERATED DELAND GROUND WATER BY "ORTHOPHENANTHROLINE ONLY"—WITH FILTRATION

membrane-filtered just prior to the colorimetric measurement in Fig. 4. Both Figs. 3 and 4 show very similar results. The values of ferrous iron obtained at 10 minutes of both Figs. 3 and 4 are quite comparable to those obtained using the batho-phenanthroline method. It can be seen from both Figs. 3 and 4 that the values for ferrous iron which were obtained increased with time. The increase in the apparent amount of ferrous iron is greater as the amount of ferrous iron decreases.

The results presented in Table 9 were also obtained from the same experiment as those shown in Figs. 3 and 4. However, the ferrous iron determinations were made by the "ortho-phenanthroline only" method. The fixed samples were filtered through membrane filters immediately after all reagents had been added. The indicated reading time refers to the period of time after filtration at which colorimetric measurements were made. The results show only very slight increases in the amounts of apparent ferrous iron as the time interval for color development increase. The values obtained at each time interval also show good agreement with those obtained by the "bathophenanthroline" method.

The effect of time on bathophenanthroline color development with aerated Deland ground water is shown in Table 10. In contrast with the ortho-phenanthroline color development, there is a slight decrease in ferrous iron as the time for color development increases.

The accuracy of the "ortho-phenanthroline only" method, with filtration and a 10 minute color development time was compared with the "bathophenanthroline" method. A ferrous iron sample was prepared by adding a known concentration of ferrous ammonium sulfate stock solution to un-aerated ground water obtained from both Deland and Champaign, Illinois. Natural water was added to 10 ml. or less of the stock solution to make a

Table 9

EFFECTS OF TIME ON ORTHO-PHENANTHROLINE COLOR DEVELOPMENT WHEN FILTERED IMMEDIATELY

Sample No.	Ferrous Iron Present - mg/l					Total Iron mg/l
	Bath.	"Orthophenanthroline only"				
		10 min.	30 min.	6 hrs.	24 hrs.	
1	3.36	3.16	3.22	3.24	3.22	4.80
2	3.36	3.48	3.48	3.56	3.56	4.45
3	2.87	2.96	2.92	2.96	2.96	-
4	2.30	2.46	2.44	2.44	2.46	4.80
5	1.96	2.00	1.98	2.00	2.02	-
6	1.50	1.60	1.46	1.52	1.55	-
7	1.10	1.08	1.06	1.10	1.10	4.45
8	0.90	0.87	0.85	0.85	0.85	-
9	0.62	0.64	0.64	0.66	0.66	-
10	0.50	0.47	0.47	0.48	0.49	4.45

Bath: bathophenanthroline

Total Iron: ortho-phenanthroline (11th Ed. Standard Method).

Table 10

EFFECTS OF TIME ON BATHOPHENANTHROLINE COLOR DEVELOPMENT

Sample	Ferrous Iron (mg/l) Reading Time			Total Iron mg/l
	10 min.	18 hrs.	48 hrs.	
1	3.32	3.17	3.15	4.45
2	2.92	2.73	2.68	4.45
3	1.96	1.74	1.74	-
4	1.34	1.16	1.18	4.80
5	0.94	0.85	0.80	-
6	0.66	0.60	0.60	4.80
7	0.48	0.48	0.42	-
8	0.36	0.33	0.30	-
9	0.26	0.25	0.24	4.45

Total Iron: Ortho-phenanthroline (11th Ed. Standard Method)

total volume of 1.0 liter. The concentration of ferrous iron in the unaerated natural water, stock solution, and in prepared mixture was determined and compared with calculated values. The calculated values of ferrous iron in the mixture solution were obtained by adding the experimental values obtained from the raw water and the standard solution. Either duplicate or triplicate analyses were made on each sample. The results are shown in Table 11. It can be seen that the experimental values and the calculated values of both the "ortho-phenanthroline only" method and the bathophenanthroline method are very comparable; the differences are well within the experimental errors and precisions which can be observed from the values obtained from the replicates of the analysis.

Table 12 shows the results of determining ferrous iron by the "ortho-phenanthroline only" method after which the fixed samples were filtered through either a membrane filter and fine Whatman No. 40 filter paper. The water sample used was aerated Cisco, Illinois, ground water. After the samples had been fixed and filtered, a period of 30 minutes was allowed for color development so as to obtain the maximum color development and compare the stability of the ortho-phenanthroline color developed. The results presented in Table 12 show that the method wherein the samples were filtered through the Whatman filter paper give higher values when compared to both the method where the samples were filtered through a membrane filter and the bathophenanthroline method. However, the method in which the samples were filtered through Whatman filter paper before being fixed showed good agreement with the bathophenanthroline method.

Table 11

RESULTS OF FERROUS IRON DETERMINATION IN THE MIXTURE OF RAW WATER AND STANDARD IRON SOLUTION

Raw Water Sources		Experimental Values: Raw mg/l (1)		Standard mg/l (2)		Mixture of Raw and Standard (3)		Calc. Values: Raw + Standard mg/l (1 + 2)	
		O	B	O	B	O	B	O	B
A)	Deland	3.64	3.60	1.96	1.98	5.85	5.80	5.60	5.58
		3.76	3.70	1.98	2.10	5.81	5.80	5.74	5.80
	Average	3.70	3.65	1.97	2.04	5.83	5.80	5.67	5.69
B)	Champaign	1.58	1.58	0.97	0.99	2.55	2.83	2.55	2.57
		1.67	1.50	0.97	0.98	2.60	2.80	2.64	2.48
		1.67	-	0.98	-	2.60	-	-	-
	Average	1.63	1.54	0.97	0.98	2.60	2.82	2.60	2.52

O: "Ortho-phenanthroline only" method and filtered through membrane filters within 10 min.

B: bathophenanthroline.

Table 12

RESULTS OF FERROUS IRON DETERMINATION (AT INTERVALS)

IN AERATED CISCO GROUND WATER

Time after Aeration-min.	Ferrous Iron - mg/l				
	0-3	0-4	0-2	0-1	B
Before Aeration	2.28	2.48	2.20	1.95	2.32
0	2.05	2.20	1.56	1.80	1.74
10	1.20	1.10	0.84	0.78	0.83
20	0.62	0.62	0.42	0.34	0.43
30	0.48	0.60	0.35	0.16	0.25
40	0.34	0.57	0.22	0.09	0.10
55	0.30	0.41	0.15	0.04*	0.08
70	0.26	0.36	0.13	0.04*	0.06
85	0.22	0.33	0.10	0.04*	0.04

Ferrous Iron:

0: "orthophenanthroline only" method.
3: fixed samples, filtered immediately with Whatman filter and read after 30 min.
4: fixed samples, filtered after 30 min. with Whatman filter and read
2: samples filtered with Whatman filter then fixed and read after 30 min.
1: fixed samples, filtered immediately with membrane filter.
B: bathophenanthroline method

* Not reliable due to lack of sensitivity of the instrument at this range.

B. Redox Potential Measurements

The results of redox potential measurements and other characteristics for the 31 plants which they study had covered are presented in Table 13. At each plant, analyses were made on water samples collected at three different stages of treatment, i.e., raw, aerated (before filtration), and finished (after filtration). The waters are separated into two groups; the first group either received no chlorine prior to filtration or if chlorine was added, it could not be detected during treatment, the second group showed an appreciable amount of chlorine residual present prior to filtration. The waters in each group arelisted in Table 13 in order of increasing amounts of total iron remaining in the finished water. The redox potential data are given in millivolts (mv) based on an "adjusted pH" for 7.0 and the standard hydrogen electrode. A correction factor of +250 mv. was used for conversion from the calomel to the hydrogen reference electrode. Since pH also affects redox potential measurements, redox potentials are referenced to a single pH for purposes of comparison. In this study pH 7.0 was used as the reference. Since the pH values of all the waters sampled were near 7.0, only a small correction was required for each water. The correction factors which were applied in converting the measured values to pH 7.0 were determined from redox data obtained using acidified samples (see Appendix B). It was found that the correction factor for raw water was 80 mv. per pH unit while 60 mv. per pH unit was the factor for the aerated and finished waters. For those waters which had pH values higher than 7.0, the corrections would be added to the measured values and vice versa. The redox potential data are reported to the nearest 10 mv. For example, if the measured redox potential of a raw water with a pH of 7.3 was 170 mv, the "adjusted" values would be 170 mv. plus 24 mv. or 194 mv. It would be reported as 190 mv.

Table 13

REDOX POTENTIALS (ORP) AND OTHER CHARACTERISTICS OF ILLINOIS GROUND WATERS AT THREE STAGES OF TREATMENT PROCESSES

(LISTED IN THE ORDER OF MAGNITUDES OF TOTAL IRON REMAINING)

Town (x)*1	1 ORP (Adjusted)-mv.			2 Ferrous Iron-mg/l			3 Total Iron-mg/l			4 Dissolved Oxygen-mg/l			5 C.O.D.-mg/l	
	Raw	Aer.	Fin.	Raw	Aer.	Fin.	Raw	Aer.	Fin.	Raw	Aer.	Fin.	Raw	Fin.
No Chlorine														
Heyworth(A)	190	330	730	0.68	0.16	0.08	0.60	0.52	0.08	0.0	8.3	8.8	1.0	1.0
St. Joseph(A)*2	190	520	480	1.78	0.35	0.08	1.94	1.72	0.08	0.0	8.0	5.3	9.1	8.1
Atwood(A)*2	160	-	520	2.58	-	0.10	2.60	-	0.08	0.0	-	0.3	13.8	16.2
Fairmount(A)	160	-	380	1.82	1.85	0.12	1.84	2.20	0.10	0.0	-	0.2	7.3	5.3
Mahomet(A)	160	440	450	2.0	0.10	0.04	2.2	2.12	0.16	0.1	9.2	6.5	3.8	6.3
Broadlands(A)	200	340	290	1.20	0.62	0.14	1.44	1.36	0.16	0.1	6.3	0.2	18.1	19.9
Bethany(B)	90	460	450	2.09	0.55	0.11	2.12	1.92	0.24	0.0	8.4	0.3	11.9	11.2
Walnut(A)	190	-	380	2.45	0.60	0.24	2.64	2.68	0.26	0.4	9.1	3.0	8.8	7.9
Chatsworth(A)	-	390	410	1.10	0.08	0.05	1.28	1.32	0.28	0.0	8.4	0.7	11.7	10.8
Argent(B)	130	300	2.70	1.20	0.18	0.11	1.36	1.28	0.28	0.1	7.6	0.3	10.6	12.4
Tremont(A)*2	100	220	300	3.42	0.36	0.10	3.60	3.00	0.42	0.0	8.2	0.0	12.1	12.5
Emden(B)	120	250	220	2.60	0.88	0.21	2.96	2.64	0.48	0.0	8.4	0.2	9.8	10.6
Findlay(C)	120	250	170	4.45	1.65	0.59	4.72	4.48	0.60	0.0	6.6	0.0	29.5	28.1
Cisco(C)*2	120	230	220	4.10	1.80	0.60	4.24	4.10	0.64	0.3	7.2	0.4	25.1	25.5
Deland(C)*2	110	310	270	4.58	1.44	0.56	4.68	4.00	0.68	0.0	7.0	0.0	48.4	40.0
Danvers(C)*2	80	310	190	2.28	1.00	0.26	2.80	2.72	0.82	0.0	7.4	0.3	50.4	48.8
Tolono(C)	350	480	260	0.90	0.75	0.92	1.08	2.58	1.02	0.20	7.6	0.1	36.0	37.6
Wapella(C)*2	80	230	140	4.98	0.76	0.79	5.00	4.52	1.04	0.0	7.0	0.1	12.5	10.8
Roxana(C)	60	130	680	15.2	8.20	0.33	16.0	13.9	1.62	0.0	7.0	6.4	43.6	37.7
Oakwood(A)	150	390	400	2.8	0.55	0.35	3.28	2.28	2.75	0.6	9.0	5.5	22.9	21.8
Wyanet(C)	120	290	310	4.50	0.48	0.33	4.72	3.08	3.32	0.2	4.8	3.8	17.8	18.6
Windsor(C)	130	-	250	6.85	-	1.83	8.48	-	4.36	0.0	-	6.8	49.4	50.2
With Chlorine														
Edwardsville(A)	140	170	540	1.89	0.90	0.08	2.14	1.84	0.16	0.6	8.4	9.1	2.8	1.6
Morton(A)	90	650	590	2.78	0.50	0.08	3.00	3.20	0.28	0.8	9.9	1.3	12.0	12.7
Forrest(B)	-20	400	450	21.4	0.28	0.04	26.0	3.16	0.16	0.0	7.8	2.0	97+	13.3
El Paso(A)	190	720	750	1.02	0.30	0.15	1.60	1.78	0.40	0.0	10.2	6.5	10.4	10.8

Table 13 (Continued)

Town (x)*1	6 Nitrate*3			7 pH			8 Temperature-°C			9 Residual Chlorine-mg/l		
	Raw	Aer.	Fin.	Raw	Aer.	Fin.	Raw	Aer.	Fin.	Raw	Aer.	Fin.
No Chlorine												
Heyworth(A)	S	S	S	7.30	7.80	7.80	13.0	13.50	13.5			
St. Joseph(A)*2	N	N	S	7.50	7.50	7.55	14.0	14.5	15.0			
Atwood(A)*2	N	-	S	7.10	-	7.40	14.2	-	15.2			
Fairmount(A)	N	N-	S	7.35	7.40	7.50	13.0	13.5	13.5			
Mahomet(A)	N	M	M	6.90	7.35	7.20	14.0	14.0	14.0			
Broadlans(A)	N	N	M	7.50	7.55	7.60	13.0	15.0	15.0			
Bethany(B)	N	N	S	7.20	7.75	7.80	15.0	15.0	15.0			
Walnut(A)	N	N	M	7.25	7.45	7.45	12.2	13.0	13.2			
Chatsworth(A)	S	M	H	7.45	7.70	7.80	14.0	14.8	15.0			
Argenta(B)	N	N	M	7.50	7.60	7.60	13.5	14.0	14.0			
Tremont(A)*2	N	N	M	6.90	7.40	7.55	13.5	13.8	15.0			
Emden(B)	S	S	H	7.10	7.50	7.45	13.5	14.0	14.0			
Findlay(C)	N	S	M	7.20	7.55	7.55	15.2	16.0	16.5			
Cisco(C)*2	N	N	M	7.00	7.20	7.10	14.0	14.0	14.0			
Deland(C)*2	S	S	M	6.70	7.30	7.35	13.2	15.0	16.0			
Danvers(C)*2	N	S	S	7.40	7.90	7.80	13.8	14.2	18.5			
Tolono(C)	N	N	S	7.50	7.55	7.60	16.0	16.0	16.0			
Wapella(C)*2	S	S	M	6.85	7.40	7.50	12.5	14.0	14.2			
Roxana(C)	N	S	M	6.80	7.10	7.10	15.2	16.0	16.8			
Oakwood(A)	N	N	M	7.50	7.80	7.80	13.5	15.0	15.0			
Wyanet(C)	N	S	S	7.40	7.45	7.50	12.0	13.0	13.5			
Windsor(C)	S	-	S	7.00	-	7.25	16.0	-	17.2			
With Chlorine												
Edwardsville(A)	H	H	H	7.10	7.40	7.75	15.2	16.2	19.0	0	0	0.3
Morton(A)	S	S	M	7.30	7.70	7.70	14.0	14.0	16.0	0	-	0.1
Forrest(B)	S	H	H	8.00	7.10	7.35	14.0	14.2	15.5	0	-	1.0
El Paso(A)	N	S	M	7.10	8.00	7.60	13.0	13.2	14.0	0	3.0	1.75

Table 13 (Continued)

Town (x)*1	1 ORP (Adjusted)-mv.			2 Ferrous Iron-mg/l			3 Total Iron-mg/l			4 Dissolved Oxygen-mg/l			5 C.O.D.-mg/l	
	Raw	Aer.	Fin.	Raw	Aer.	Fin.	Raw	Aer.	Fin.	Raw	Aer.	Fin.	Raw	Fin.
Hudson(B)	90	280	720	1.98	0.73	0.08	2.60	2.32	0.44	0.0	7.1	9.1	36.2	36.7
Arcola(C)	250	650	490	5.02	1.00	0.40	5.08	3.52	0.62	0.4	9.3	0.4	22.6	23.4
La Moille(C)	160	610	280	1.50	0.48	0.70	1.68	0.50	1.04	0.2	8.3	3.5	12.9	13.2
Marine(C)	100	690	710	4.18	1.07	0.58	4.36	4.27	1.12	0.0	9.6	8.3	37.0	36.5
Warrensberg(C)	140	670	680	3.60	1.16	1.04	3.68	3.40	1.44	0.0	5.5	8.9	28.1	28.9

Table 13 (Continued)

Town (x)*1	6 Nitrate*3			7 pH			8 Temperature-°C.			9 Residual Chlorine-mg/l		
	Raw	Aer.	Fin.	Raw	Aer.	Fin.	Raw	Aer.	Fin.	Raw	Aer.	Fin.
Hudson(B)	N	S	M	7.30	7.60	7.70	12.8	14.2	16.0	0	-	5.0
Arcola(C)	N	N	S	7.50	7.60	7.15	16.5	16.0	16.0	0	1.2	1.0
La Moille(C)	S	S	M	7.35	7.90	8.30	12.3	13.0	13.0	0	0.35	Nil
Marine(C)	S	S	M	7.40	7.65	7.60	13.5	14.5	15.2	0	3.0	3.0
Warrensberg(C)	N	N	-	7.00	7.50	7.50	14.0	14.0	14.0	0	2+	2+

*1 The letter in the bracket following the name of a town, here after, indicates the range of total iron remaining in finished water as obtained from Illinois Department of Public Health records.
(A): indicates iron from 0 to 0.2 mg/l
(B): indicates iron from 0.2 to 0.4 mg/l
(C): indicates iron over 0.4 mg/l

*2 Chlorine might have been applied during treatment process in these plants, but the amount was nil and could not be detected at any stage of the treatment.

*3 Nitrate content: N = nil; S = slight; M = moderate; H = high

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From the results shown in Table 13, it can be seen that the redox potentials for all waters increased as a result of aeration and either increased or decreased following filtration. The redox potential for the raw water at Tolono was unusually high, since it was not possible to collect a sample of raw water as it was being pumped from the well, the measured value was obtained on raw water which had been stored in an elevated tank. Undoubtedly, storage had affected the redox potential. The redox potential of Forrest raw waters was found to be unusually low in comparison to the other raw waters. The raw water at Forrest gave a sulfide odor during measurement. The ferrous iron concentration in the water also was found to be extremely high (over 20 mg/l) as was the C.O.D. These unusual results may be attributed to an improper sampling connection, since it was found that the pipe from which the samples were drawn has been out of service for some time and a great deal of corrosion rust was apparent. It was also found that, for waters which contained only a slight amount of residual chlorine, the redox potentials were considerably higher than those with no chlorine.

Table 13 shows that in general there is a decrease in ferrous iron in the water following aeration and a further decrease as a result of filtration. There are three cases (Tolono, Wapella and La Moille) where the amount of ferrous iron was greater in the finished water than in the aerated water, associated with this increase in ferrous iron was a significant decrease in redox potential. The amount of total iron remained constant between the raw and the aerated water but was significantly reduced by the filter. There were also some cases in which the amount of total iron increased. However, such results are not usual and may be attributed to an inadequate filtration capacity.

From records of monthly analyses made by the Illinois Department of Public Health, these same waters were divided into three classes based

on the amount of total iron remaining in the finished water. Class "A" includes those waters in which the total iron concentration in the finished water during the past few months was consistently less than 0.20 mg/l; class "B" contains those in which the iron concentration was between 0.20 5o 0.40 mg/l while those finished water containing more than 0.40 mg/l are grouped in class "C". For purposes of comparison, the designated letter for each water is indicated in the brackets following the name of each town (Table 13). It can be seen that the values of total iron remaining in the finished water as obtained in this study are, for the most part, comparable to the results obtained by the Illinois Department of Public Health. The concentration of dissolved oxygen in the raw waters were usually zero with only a few exceptions and may have been due to an air leak in the pumping system or connection. In almost all of the plants surveyed, coke tray aeration was the unit process employed. The dissolved oxygen content after aeration in all plants was sufficiently high, in the range of 7 to 8 mg/l. The concentration of dissolved oxygen, therefore did not appear to be a limiting factor at the plants visited in this study. However, in many cases there were substantial reduction of dissolved oxygen in the filters. The depletion of oxygen in passing through the filter often resulted in poor iron removal.

From the chemical oxygen demand (C.O.D.)* of the raw and finished waters shown in Table 13, it appears that in most cases, the C.O.D. of water was not significantly affected by filtration. The values of C.O.D. in raw and finished water remain constant. An interesting trend is evident from the data in Table 13. Where the C.O.D. is high, the redox potential is low and vice versa.

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* The values of C.O.D. reported herein are corrected for chlorides.

With the method of nitrate determination, employed, only crude quantitative estimates could be obtained. However, it was possible to compare the nitrate content at each stage of treatment. From the nitrate data shown in Table 13, it is evident that in many plants there was a significant increase in nitrate content in the finished water. This corresponded to a decrease in dissolved oxygen. In some cases there was also an increase in the nitrate content between the raw and the aerated waters. This may have been due to an abundant slime growth which was often observed in the coke tray aeration units.

Table 13 shows that the pH of water increased when water was aerated. The increase in pH from the raw to the aerated water were usually greatest where the raw water had a high gas (CO_2) content.

The temperature of all the raw waters samples range from 20°C to 16°C with most values between 13°C and 14°C. Slight increases in temperature from the raw to the finished water were noticed; usually within 1°C. Such a small temperature change would have little effect on the treatment processes or chemical behavior of the waters.

The increases in redox potentials (adjusted to pH 7.0) from raw to aerated and the corresponding changes in other characteristics are shown in Table 14. The waters are listed in the order of increasing redox potentials so that the order of change in other characteristics can be observed. All changes in redox potentials and other characteristics are computed as differences from the raw water values i.e., by subtracting the raw water values from the aerated water values. The percent increase in oxidized iron was obtained from the percent differences in the ratio of ferrous iron to total iron in the raw and the aerated waters. From the results shown in Table 14 it appears that there is no correlation between the changes in redox potential, the changes in oxidized iron, the efficiency

Table 14

RELATIONSHIP OF CHANGES IN REDOX POTENTIALS TO CHANGES IN OTHER CHARACTERISTICS FROM RAW TO AERATED WATERS

[Listed in the order of changes in redox potential(ΔORP)]

Town	Δ ORP (adjusted) mv	Δ Ferrous mg/l	% change in Oxidized Iron	Ferrous Remaining in Fin. mg/l	Δ D.O mg/l	Δ Nitrate*	Δ ph	Δ temp. °C	Δ Residual Chlorine mg/l
No Chlorine									
Bethany(B)	+370	-1.54	+70	0.11	+ 8.4	0	+0.55	0	-
St. Joseph(A)	+330	-1.43	+71	0.08	+ 8.0	0	0	+0.5	-
Mahomet(A)	+280	-1.90	+86	0.04	+ 9.2	0	+0.43	+0.5	-
Oakwood(A)	+240	-2.25	+61	0.35	+ 8.4	0	+0.30	+1.5	-
Danvers(C)	+230	-1.28	+44	0.26	+ 7.4	+	+0.50	+0.4	-
Deland(C)	+200	-3.14	+62	0.56	+ 6.9	0	+0.60	+2.2	-
Argenta(B)	+170	-1.02	+74	0.11	+ 7.5	0	+0.10	+0.5	-
Wyanet(C)	+170	-4.02	+80	0.33	+ 4.6	+	+0.05	+1.0	-
Wapella(C)	+150	-4.22	+83	0.79	+ 7.0	0	+0.55	+1.5	-
Heyworth(A)	+140	-0.52	+69	0.08	+ 8.3	0	+0.50	+0.5	-
Broadlands(A)	+140	-0.58	+38	0.14	+ 6.2	0	+0.05	+2.0	-
Emden(B)	+130	-1.72	+55	0.21	+ 8.4	0	+0.40	+0.5	-
Findlay(C)	+130	-2.80	+58	0.59	+ 6.6	+	+0.35	+0.8	-
Tolono(C)	+130	-0.15	+54	0.92	+ 7.4	0	+0.05	0	-
Tremont(A)	+120	-3.06	+83	0.10	+ 8.2	0	+0.50	+0.3	-
Cisco(C)	+110	-2.30	+53	0.60	+ 6.9	0	+0.20	0	-
Roxana(C)	+70	-7.00	+36	0.33	+ 7.0	+	+0.30	+0.8	-
With Chlorine									
Marine(C)	+590	-3.11	+71	0.58	+ 9.6	0	+0.25	+1.0	+3.0
Morton(A)	+560	-2.28	+77	0.08	+ 9.1	0	+0.40	0	-
El Paso(A)	+530	-0.72	+47	0.15	+10.2	+	+0.90	+0.2	+3.0
Warrensberg(C)	+530	-2.44	+64	1.04	+ 5.5	0	+0.50	0	+3.0
La Moille(C)	+450	-1.02	+57	0.70	+ 8.1	0	+0.55	+0.7	+0.35
Forrest(B)	+420	-21.12	+74	0.04	+ 7.8	++	-0.90	+0.2	-
Arcola(C)	+400	-4.02	+71	0.40	+ 8.9	0	+0.10	+0.5	+1.2
Hudson(B)	+190	-1.25	+45	0.08	+ 7.1	+	+0.30	+1.4	-
Edwardsville(A)	+30	-0.99	+39	0.08	+ 7.8	0	+0.30	+0	0

*Degree of increase in nitrate: 0 = nil; + = slight increase; ++ = high increase.

of iron removal or any other characteristics presented. However, it should be noted that for water with no chlorine, if the increase in redox potentials was less than +140 mv., the percent increase in oxidized iron was lower than 60 percent, with the exception of Tremont. In the case of Danvers, the increase in redox potentials was 230 mv while the increase in oxidized iron was only 44 percent; however, the plant operator stated that a slight amount of chlorine had been added to the raw water. Hence, the increase in redox potentials may have been due to the addition of chlorine. In many cases the aerated water redox potentials were obtained at stages in the treatment which varied from one plant to another plant. For example, in some cases the aerated water redox potential was obtained almost immediately after aeration, and in other cases they were obtained just before filtration. The procedures for obtaining redox potentials of the aerated waters then cannot be regarded as entirely consistent.

A comparison of changes in redox potentials with changes in other characteristics from raw to finished waters are shown in Table 15. All the changes are computed using the raw water values as reference. It can be seen that in both groups of water, with an without chlorine, where the increase in redox potentials from raw to finished was less than 200 mv. the efficiency of iron removal was relatively low. Of all 13 cases where the increase in redox potentials was less than 200 mv, there was only one plant (Broadlands) which had less than 0.20 mg/l of iron remaining in the effluent; and two cases (Walnut with 190 mv and Argenta with 140mv) which had iron remaining between 0.20 to 0.40 mg/l; the rest of the plants contained iron in concentrations greater than 0.40 mg/l in the finished water. In the case of Broadlands, however, strongly reducing conditions in the filters existed as evidenced by the depletion of oxygen, a significant increase in the nitrate content and the slight increase in C.O.D. A similar phenomena

Table 15

COMPARISON OF CHANGES IN REDOX POTENTIALS WITH CHANGES IN OTHER CHARACTERISTICS FROM RAW TO FINISHED WATERS

[Listed in the decreasing order of changes in redox potentials (ΔORP)]

Town	1 ΔORP (Adjusted) mv δ	2 Ferrous Iron Amount Change mg/l	2 Ferrous Iron Amount Remaining mg/l	2 Ferrous Iron % Change	3 Total Iron Amount Change mg/l	3 Total Iron Amount Remaining mg/l	3 Total Iron % Change
No Chlorine							
Roxana(C)	620	-14.87	0.33	-98.2	-14.38	1.62	-91
Heyworth(A)	540	- 0.60	0.08	-88.5	- 0.52	0.08	-86
Atwood(A)	360	- 2.48	0.10	-96.0	- 2.52	0.08	-97
Bethany(B)	360	- 1.98	0.11	-94.5	- 1.88	0.24	-88
St. Joseph(A)	290	- 1.70	0.08	-95.5	- 1.86	0.08	-96
Mahomet(A)	240	- 1.96	0.04	-98.0	- 2.04	0.16	-93
Oakwood(A)	250	- 2.45	0.35	-87.5	- 0.53	2.75	-16
Fairmount(A)	220	- 1.70	0.12	-93.5	- 1.74	0.10	-95
Tremont(A)	200	- 3.32	0.10	-97.2	- 3.18	0.10	-88
Walnut(A)	190	- 2.21	0.24	-90.5	- 2.38	0.26	-90
Wyanet(C)	190	- 4.17	0.33	-92.8	- 1.40	3.32	-30
Deland(C)	160	- 4.02	0.56	-98.5	- 4.00	0.68	-85
Argenta(B)	140	- 1.09	0.11	-90.5	- 1.08	0.28	-79
Windsor(C)	120	- 5.02	1.83	-73.5	- 4.12	4.36	-49
Danvers(C)	110	- 2.02	0.26	-88.5	- 1.98	0.82	-71
Emden(B)	100	- 2.34	0.21	-92.0	- 2.48	0.48	-84
Cisco(C)	100	- 3.50	0.60	-95.2	- 3.60	0.64	-85
Broadlands(A)	90	- 1.06	0.14	-88.5	- 1.28	0.16	-89
Wapella(C)	60	- 4.19	0.79	-84.5	- 3.96	1.04	-79
Findlay(C)	50	- 3.86	0.59	-87.0	- 4.12	0.60	-87
Tolono(C)	-90	+ 0.02	0.92	- 2.2	- 0.06	1.02	- 6
With Chlorine							
Hudson(B)	630	- 1.90	0.08	-96	- 2.16	0.44	-83
Marine(C)	610	- 3.60	0.58	-86	- 3.24	1.12	-74
El Paso(A)	560	- 0.87	0.15	-85	- 0.87	0.40	-85
Warrensberg(C)	540	- 2.56	1.04	-71	- 2.56	1.44	-71
Morton(A)	500	- 2.70	0.08	-97	- 2.72	0.28	-91
Forrest(B)	270	-21.36	0.04	-99+	-25.84	0.16	-99+
Edwardsville(A)	400	- 0.99	0.08	-52	- 1.98	0.16	-93
Arcola(C)	240	- 4.62	0.40	-92	- 4.46	0.62	-88
La Moille(C)	120	- 0.80	0.70	-53	- 0.64	1.04	-38

Table 15 (Continued)

Town	4 Δ D.O. mg/l	5 Δ Nitrate*	6 Δ C.O.D. mg/l	7 Δ pH	8 Δ Temp. °C	9 Δ Residual Chlorine mg/l
No Chlorine						
Roxana(C)	+6.4	+++	-5.9	+0.30	+1.5	-
Heyworth(A)	+8.8	0	0	+0.50	+0.5	-
Atwood(A)	+0.3	+	+2.4	+0.30	+1.0	-
Bethany(B)	+0.3	+	-0.7	+0.50	0	-
St. Joseph(A)	+5.3	+	-1.0	+0.05	+1.0	-
Mahomet(A)	+6.4	++	+2.5	+0.30	0	-
Oakwood(A)	+4.9	++	-1.1	+0.30	+1.5	-
Fairmount(A)	+0.2	+	-2.0	+0.15	+0.5	-
Tremond(A)	0.0	++	+0.4	+0.65	+1.5	-
Walnut(A)	+2.6	++	-0.9	+0.20	+1.0	-
Wyanet(C)	+3.6	+	+0.8	+0.10	+1.5	-
Deland(C)	0.0	++	-8.4	+0.65	+2.8	-
Argenta(B)	+0.2	++	+1.8	+0.10	+0.5	-
Windsor(C)	+6.8	0	+0.8	+0.25	+1.2	-
Danvers(C)	+0.3	+	-0.6	+0.40	+4.7	-
Emden(B)	+0.2	++	+0.7	+0.35	+0.5	-
Cisco(C)	+0.1	++	-0.4	+0.10	0	-
Broadlands(A)	+0.1	++	+1.1	+0.10	+2.0	-
Wapella(C)	+0.1	+	-1.7	+0.65	+1.7	-
Findlay(C)	0	++	-1.4	+0.35	+0.3	-
Tolono(C)	+0.1	+	+1.6	+0.10	0	-
With Chlorine						
Hudson(B)	+9.1	+	+0.5	+0.40	+3.2	5.0
Marine(C)	+8.3	++	-0.5	+0.20	+1.7	3.0
El Paso(A)	+6.5	++	+0.4	+0.50	+1.0	1.75
Warrensberg(C)	+8.9	—	+0.8	+0.50	-0	2+
Morton(A)	+0.5	+	+0.7	+0.40	+2.0	0.1
Forrest(B)	+2.0	++	84+	-0.65	+1.5	1.0
Edwardsville(A)	+8.5	+	-1.2	+0.65	+3.8	0.3
Arcola(C)	0	+	+0.8	-0.35	-0.5	1.0
La Moille(C)	+3.3	++	+0.3	+0.95	+0.7	nil

* Degree of increase in nitrate: 0 = nil; + = slight; ++ = high.

was also observed at Argenta where a heavy slime growth in the filter was noted.

For those waters which contained chlorine, the increases in redox potentials showed a tendency to vary with the increase in amount of residual chlorine. Those waters which contained no chlorine, and where the increase in potentials were greater than +200 mv, only two plants (Roxana and Oakwood) showed a total iron content in the finished water greater than 0.40 mg/l. However, the ferrous iron remaining in both cases was still less than 0.4 mg/l. In the case of Oakwood, the deficiency of the filter was quite apparent; the reduction of total iron from raw to finished water was only 16 percent, whereas the reduction in ferrous iron content was over 87 percent. In the case of Roxana, where the raw water had an unusually high total iron content, the decrease in ferrous and total iron content from raw to finished water was over 90 percent.

A comparison of changes in redox potentials with changes in other characteristics from aerated to finished waters is shown in Table 16. The treatment plants are listed in the order of increasing redox potentials for both groups. For the group with no chlorine residual, it can be seen that when the decrease in redox potential during filtration is greater than -50 mv poor efficiency in iron removal by filters is also noted. In two cases (Arcola and La Moille) where chlorine was present, the decrease in redox potentials in the filters of -160 mv and -330 mv corresponded to poor efficiency in iron removal. In all three cases (Wapella, Tolono and La Moille) where the amount of ferrous iron increased upon passing through the filters there was also a corresponding decrease in redox potentials. However, those plants which showed an increase in redox potentials from aerated to finished water did not always show satisfactory iron efficiency. There is no definite correlation between the changes in redox potentials

Table 16

COMPARISON OF CHANGES IN REDOX POTENTIALS WITH CHANGES IN OTHER CHARACTERISTICS FROM AERATED TO FINISHED WATER

[Listed in the decreasing order of changes in redox potentials (ΔORP)]

Town	1 ΔORP (Adjusted) mv	2 Ferrous Iron Amount Change mg/l	2 Ferrous Iron % Change	3 Total Iron Amount Change mg/l	3 Total Iron Amount Remaining mg/l	3 Total Iron % Change
No Chlorine						
Roxana(C)	+550	-7.87	-96	-12.28	1.62	-88
Heyworth(A)	+400	-0.08	-50	-0.44	0.08	-85
Tremont(A)	+80	-0.26	-72	-2.58	0.10	-86
Chatsworth(B)	+20	-0.03	-38	-1.04	0.28	-79
Wyanet(C)	+20	-0.15	-31	+0.24	3.32	+8
Mahomet(A)	+10	-0.06	-60	-1.96	0.16	-92
Oakwood(A)	+10	-0.2	-36	+0.47	2.75	+21
Bethany(B)	-10	-0.44	-80	-1.68	0.24	-88
Cisco(C)	-10	-1.20	-65	-3.46	0.64	-84
Argenta(B)	-30	-0.07	-39	-1.0	0.28	
Emden(B)	-30	-0.67	-76	-2.16	0.48	-78
St. Joseph(A)	-40	-0.27	-77	-1.64	0.08	-95
Deland(C)	-40	-0.88	-60	-3.32	0.68	-83
Broadlands(A)	-50	-0.48	-72	-1.20	0.16	-88
Findlay(C)	-80	-1.06	-64	-3.88	0.60	-87
Wapella(C)	-90	+0.03	+4	-3.48	1.04	-77
Danvers(C)	-120	-0.74	-74	-1.90	0.82	-70
Tolono(C)	-220	+0.17	+23	-1.56	1.02	-60
With Chlorine						
Hudson(B)	+440	-0.65	-89	-1.88	0.44	-81
Edwardsville(A)	+370	-0.82	-91	-1.68	0.16	-91
Forrest(B)	+50	-0.24	-86	-3.00	0.16	-95
El Paso(A)	+30	-0.15	-50	-1.38	0.40	-78
Marine(C)	+20	-0.49	-46	-3.14	1.12	-74
Warrensberg(C)	+10	-0.12	-10	-1.96	1.44	-58
Morton(A)	-60	-0.42	-84	-2.92	0.28	-91
Arcola(C)	-160	-0.60	-60	-2.90	0.62	-82
La Moille(C)	-330	+0.32	+46	-0.46	1.04	-30

Table 16 (Continued)

Town	4 Δ D.O. mg/l	5 Δ Nitrate*	6 Δ pH	7 Δ Temp. °C	8 Δ Residual Chlorine mg/l
No Chlorine					
Roxana(C)	-0.6	+	0.00	+0.8	-
Heyworth(A)	+0.5	0	0.00	0.0	-
Tremont(A)	-8.2	++	+0.15	+1.2	-
Chatsworth(B)	-7.7	++	+0.10	+0.2	-
Wyanet(C)	-1.0	0	+0.05	+0.5	-
Mahomet(A)	-2.7	0	-0.15	0.0	-
Oakwood(A)	-3.5	++	0.00	0.0	-
Bethany(B)	-8.1	+	+0.05	0.0	-
Cisco(C)	-6.8	++	-0.10	0.0	-
Argenta(B)	-7.3	++	0.00	0.0	-
Emden(B)	-8.2	++	-0.05	0.0	-
St. Joseph(A)	-2.7	+	+0.05	+0.5	-
Deland(C)	-7.0	+	+0.05	+1.0	-
Broadlands(A)	-6.1	++	+0.05	0	-
Findlay(C)	-6.6	+	0.00	+0.5	-
Wapella(C)	-6.9	4	+0.10	+0.2	-
Danvers(C)	-7.1	0	-0.10	+4.3	-
Tolono(C)	-7.5	+	+0.05	0.0	-
With Chlorine					
Hudson	+2.0	+	+0.10	+1.8	-
Edwardsville(A)	+0.7	0	+0.35	+2.8	+0.3
Forrest(B)	-5.8	++	+0.25	+1.3	-
El Paso	-3.7	+	+0.40	+0.8	-1.25
Marine(C)	-1.3	+	-0.05	+0.7	0
Warrensberg	+3.4	-	0.00	0.0	-
Morton(A)	-8.6	+	0.00	+2.0	-
Arcola(C)	-8.9	+	-0.45	0.0	-0.2
La Moille(C)	-4.8	+	+0.40	0.0	-0.35

* Degrees of increase in nitrate: 0 = nil; + = slight; ++ = high.

and the changes in percent decrease in ferrous or ferric iron during filtration.

Table 17 shows the redox potentials and other characteristics of finished waters in the order of decreasing redox potential. It is apparent that there is a general trend relating redox potentials to the amount of both ferrous and total iron remaining. Those finished waters which have high redox potentials, in general, have low both ferrous and total iron content and vice versa. The water which had a high redox potential also had a relatively higher dissolved oxygen content and lower chemical oxygen demand than the water with a low redox potential. It is particularly significant that all waters including both chlorinated and unchlorinated with redox potentials less than 270 mv contained more than 0.40 mg/l total iron. For those waters with redox potentials over 270 mv and a ferrous iron content greater than 26 percent of the total iron, all showed a total iron concentration less than 0.30 mg/l in the effluent. For waters which contained residual chlorine, the redox potentials usually were high regardless of the amount of ferrous or ferric iron remaining.

In Fig. 5, the raw water chemical oxygen demand is plotted against the raw water redox potentials for each treatment plant visited. Each plotted point also indicates the corresponding total iron remaining in the plant effluent as obtained in this survey. The letters in brackets after each plotted point indicate the values of the total iron remaining in plant effluent as found in the monthly analysis by the Illinois Public Health Department. The values shown are the average values of the past months from January to August 1961. The State values provide long-term average values to which the analyses made in this study can be compared. It was found that, in general, the values obtained in this study fall within the ranges of the State values. From the plot shown in Fig. 5, no direct

Table 17

COMPARISON OF REDOX POTENTIALS WITH OTHER CHARACTERISTICS IN FINISHED WATER

[Listed in the order of redox potentials (ORP) of finished water]

Town	ORP (Adjusted) mv	Iron Remaining			D.O. mg/l	C.O.D. mg/l	Nitrate*	pH	Residual Chlorine mg/l
		Ferrous mg/l	Total mg/l	% Ferrous					
No Chlorine									
Heyworth(A)	730	0.08	0.08	100	8.8	1.0	S	7.80	-
Roxana(C)	680	0.33	1.26	26	6.4	37.7	M	7.10	-
Atwood(A)	520	0.10	0.08	100	0.3	16.2	S	7.40	-
St. Joseph(A)	480	0.08	0.08	100	5.3	8.1	S	7.55	-
Mahomet(A)	450	0.04	0.16	25	6.5	6.3	M	7.20	-
Bethany(B)	450	0.11	0.24	46	0.3	11.2	S	7.80	-
Chatsworth(B)	410	0.05	0.28	18	0.7	10.8	H	7.80	-
Oakwood(A)	400	0.35	2.75	12	5.5	21.8	M	7.80	-
Fairmount(A)	380	0.12	0.1	100	0.2	5.3	S	7.50	-
Walnut(A)	380	0.24	0.26	93	3.0	7.9	M	7.45	-
Wyanet(C)	310	0.33	3.32	10	3.8	18.6	S	7.50	-
Tremont(A)	300	0.10	0.42	24	0.0	12.5	M	7.55	-
Broadlands(A)	290	0.14	0.16	88	0.2	19.9	M	7.60	-
Argenta(B)	270	0.11	0.28	39	0.3	12.4	M	7.60	-
Deland(C)	270	0.56	0.68	83	0.0	4.0	M	7.35	-
Tolono(C)	260	0.92	1.02	90	0.1	37.7	S	7.60	-
Windsor(C)	250	1.83	4.36	42	6.8	50.2	S	7.25	-
Emden(B)	220	0.21	0.48	44	0.2	10.6	H	6.45	-
Cisco(C)	220	0.60	0.64	93	0.4	25.5	M	7.10	-
Danvers(C)	190	0.26	0.83	32	0.3	48.8	S	7.80	-
Findlay(C)	170	0.59	0.60	99	0.0	28.1	M	7.55	-
Wapella(C)	140	0.79	1.04	76	0.1	10.8	M	7.50	-
With Chlorine									
El Paso(A)	750	0.15	0.4	38	6.5	10.8	M	7.60	1.75
Hudson(B)	720	0.08	0.44	18	9.1	36.7	M	7.70	5.0
Marine(C)	710	0.58	1.12	48	8.3	36.5	M	7.60	3.0
Warrensberg(C)	680	1.04	1.44	91	8.9	28.9	-	7.50	2+
Forrest(B)	670	0.06	0.32	19	2.0	13.3	H	7.35	1.0
Morton(A)	590	0.08	0.28	29	1.3	12.7	M	7.70	0.1
Edwardsville(A)	540	0.08	0.16	50	9.1	1.6	H	7.75	0.3
Arcola(C)	490	0.4	0.62	65	0.4	23.4	S	7.15	1.0
La Moille(C)	280	0.70	1.04	67	3.5	13.2	M	8.30	nil

* Nitrate Content: N = nil; S = slight; M = moderate; H = high.

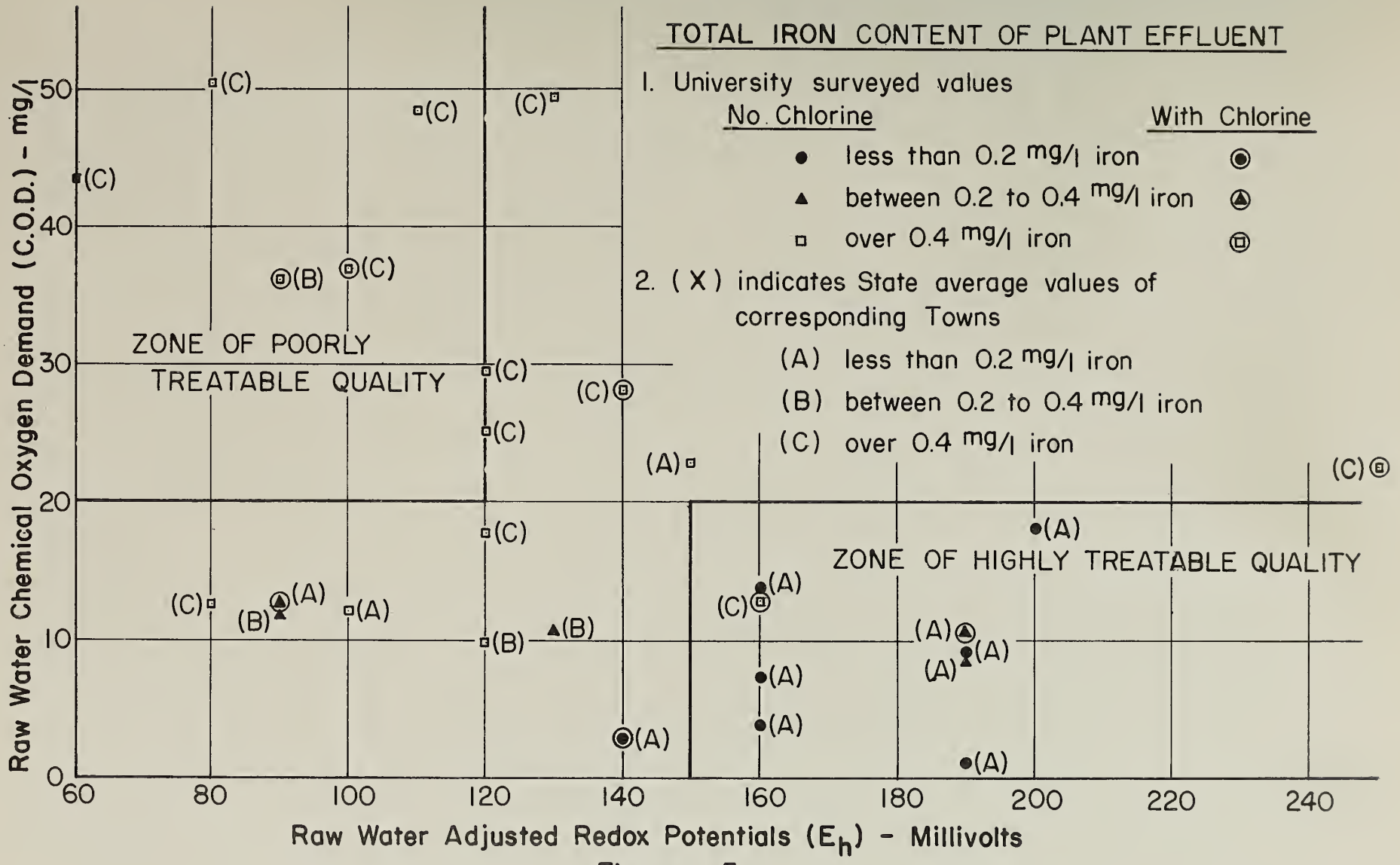

Figure 5

RELATIONSHIP OF TOTAL IRON CONTENT IN PLANT EFFLUENT
TO CHEMICAL OXYGEN DEMAND AND REDOX POTENTIALS OF RAW WATERS

correlation between C.O.D. and redox potentials can be drawn. However, it is apparent that the plotted points of those plants which normally contained less than 0.20 mg/l of iron in the effluent seem to fall in a specific region of the plot. Those plotted values for finished waters which contained more than 0.40 mg/l iron were found in a separate region. The "Zone of Highly Treatable Quality" and the "Zone of Poorly Treatable Quality" were drawn arbitrarily to indicate these respective areas. The "Zone of Highly Treatable Quality" constitutes the area of C.O.D. from 0 to 20 mg/l and where the redox potentials are above 150 mv. This implies that the treatment of those waters which have raw water C.O.D. less than 20 mg/l and raw water redox potentials above 150 mv, show high efficiency in iron removal by the conventional units used. The reverse is true in the other zone. There is one point in the "Zone of Highly Treatable Quality" where the iron remaining is indicated as "C". However, the value as obtained by the State of Illinois Department of Public Health in the month prior to this survey show the value of 0.08 mg/l iron remaining in the finished water. This plant also showed an increase in ferrous iron in the filter at the time this survey was made. Hence these might indicate that the poor quality effluent was more due to the plant operation rather than the poor water quality at the time this survey was made.

VI. DISCUSSION OF RESULTS

A. Analysis of Ferrous Iron

Since 10 ml. of ortho-phenanthroline were used in both ferrous and ferric iron determination instead of 2 ml. as recommended in the 11th Edition of Standard Methods, it can be assumed that the amount of ortho-phenanthroline present was in excess and did not limit color development. From the results shown in Table 1, it is evident that the bathophenanthroline method gives the values closest to the calculated values and was not significantly affected by the ratio of ferrous to ferric iron. The presence of ferric iron did not interfere with the determination by bathophenanthroline, since the ferrous color complex was separated from the ferric iron upon extraction with isoamyl alcohol. Therefore, the bathophenanthroline method was regarded as a reference in this study.

In contract, it can be seen that for the ortho-phenanthroline method, the experimental values of ferrous iron increased with a decreasing ratio of ferrous to ferric iron. This is likely due to the conversion of ferric to ferrous iron complex in the presence of a high percentage of ferric iron. Under this condition, the solution is not at equilibrium and the ferrous iron complex has a large stability constant as compared to the ferric iron complex (31). However, the mechanism of this reduction has not yet been fully explained. As the ratio of ferrous to ferric iron in the samples increased or when only ferrous iron existed, the experimental values by all methods of ortho-phenanthroline were quite comparable to the calculated values. It is understood that the conversion from ferric to ferrous iron might have been reduced. It is also evident that when samples were acidified and buffered or only buffered, the values of ferrous iron were consistently higher than both the calculated and bathophenanthroline values. It should be noted that lowering the pH of solutions by either

acidifying or buffering may help to increase the conversion of ferric to ferrous iron, especially where a high ratio of ferric to ferrous iron exists since the method of determination by "ortho-phenanthroline only" show lower values and agree quite well with both the calculated and bathophenanthroline method.

In the determination of total iron by the ortho-phenanthroline method (11th Edition, Standard Methods), the values obtained as shown in Table 1 are very comparable to the calculated values. Since all the iron was reduced to the form of ferrous iron by hydroxylamine hycrochloride and maintained in this stage by an excess amount of this reducing agent, the interference by ferric iron was eliminated. The values of total iron, as obtained by ortho-phenanthroline and bathophenanthroline as shown in Table 2 also showed good agreement between the two methods. It may be concluded that the method of determining total iron by ortho-phenanthroline as recommended in the 11th Edition of Standard Methods is reliable.

From the results of the ferrous iron determinations in natural water by the bathophenanthroline and various modifications of the ortho-phenanthroline methods as presented in Table 2 and Table 3, it is obvious that the values obtained by the ortho-phenanthroline methods with either acidifying or buffering were higher than both the bathophenanthroline and the "ortho-phenanthroline only" methods. The differences seem to be greater at the lower ranges of ferrous iron. In both cases, the total iron remained almost constant (with the exception being the filter effluent shown in Table 2), whereas the ferrous iron decreased gradually with time; therefore, the ratios of ferric to ferrous iron in the solutions increased with time. It then may be concluded that the interferences due to ferric iron increased at the higher ratio of ferric to ferrous iron.

Table 4 indicates results similar to those shown in Table 3. However, in this case natural water with a much higher iron concentration was used in the experiment. Results in Table 4 confirm the earlier statement that if the samples were acidified or buffered, the values of ferrous iron would be higher than both the "ortho-phenanthroline only" and the batho-phenanthroline methods. It is suspected that the methods of acidifying samples may disturb the states of iron in the solution and result in erroneously high values of ferrous iron. It is generally believe that the preservation of ferrous iron in samples can be done by acidifying the samples on the assumption that the presence of the acid tends to stabilize the original valence state of the metals(41). From the results shown from Table 1 to Table 4, it is evident that the acidified methods give values consistently higher than the bathophenanthroline and the calculated values when both ferrous and ferric iron are present. Acidification of samples therefore may lead to errors in the apparent values of ferrous iron for the same reasons which have been pointed out.

The ortho-phenanthroline method with an adjusted blank gave the lowest values of all the ortho-phenanthroline methods employed and closest to the bathophenanthroline. Though the volume of the original sample taken for each determination varied from 10 ml. to 25 ml., the effects of turbidity due to the iron floc was quite prominent. By comparing the results read against an acidified adjusted blank in which the iron floc was dissolved and the adjusted blank, it can be seen that the former showed consistently higher values. The differences were well over 1 mg/l in most cases and can be attributed to the turbidity in the adjusted blanks. Hence, in the determination of ferrous iron in the presence of a high amount of precipitated iron, special care must be taken to compensate for the error which may be caused by the turbidity as well as the color.

Since it has been noted that the time of color development was also a critical factor in the determination, a period of only about 10 minutes was allowed between the time the samples were fixed and the time color measurement was made so as to eliminate any error due to instability of color developed. It can be seen that the agreement between the method of "ortho-phenanthroline only" and the bathophenanthroline was greatly improved by using the shorter time for color development. Though the readings were made within 10 minutes to prevent any possible changes of color with time the "ortho-phenanthroline plus ammonium acetate" method still gave higher values than both the bathophenanthroline and the "ortho-phenanthroline only" method.

In an attempt to improve the "ortho-phenanthroline only" method filtration was employed to eliminate the turbidity due to the iron floc so that distilled water could be used as a colorimetric blank instead of an adjusted blank which must be made up for each corresponding sample.

From the results shown in Table 6. it is evident that the filtration method is very comparable to the adjusted blank method and the bathophenanthroline method. From the results shown in Table 7 it can be seen that filtration reduces the intensity of the color slightly and the results were lower. However, the reduction was not very significant as indicated by the percent transmittance. It appears that the reduction of the color due to filtration was well within the limit of experimental error and the benefit gained from filtration was well justified.

From the results of the effect of time on ortho-phenanthroline color development shown in Table 8, it is evident that there was an increase in the intensity of the color development with time. It can be seen from the percent changes that the increase in color intensity became greater as the ferrous iron concentration in the samples decreased and the ferric

iron concentration increased. This result also may have been due to the conversion of ferric iron to ferrous iron which forms a colored complex with ortho-phenanthroline. However, this increase in color was probably not due to the increase in ferric ortho-phenanthroline complex, since at the wavelength employed (512mμ) the ferric iron complex has very low absorbancy (21). It also was observed that the ortho-phenanthroline plus ammonium acetate method which has been recommended in the 11th Edition of Standard Methods (2) did not give a stable color as it was claimed. The results shown in Fig. 3 and Fig. 4 indicate that the ortho-phenanthroline color developed in the ferrous iron determination is not stable but changes with time. Figure 4 clearly indicates that the changes in apparent amount of ferrous iron was comparatively small at the beginning where the ferric iron was relatively low and increased gradually as the ferric iron in the samples increased. The slight changes in ortho-phenanthroline color, developed within 30 minutes, can be noted in Fig. 3. However, all values of ferrous iron which were obtained by reading at 10 and 30 minutes were very comparable to the bathophenanthroline values.

From the results of Table 9, it is interesting to note that when the sample is filtered immediately after being fixed with ortho-phenanthroline, the developed color becomes quite stable. The contrast of results between Table 9 and Fig. 4 where filtration was delayed till prior to the colorimetric readings, can be clearly observed. In another similar set of samples, the colored filtrates were permitted to stand for a period of 3 days. It was found that the increase in the indicated amount of ferrous iron was very slight. It appears that the ferric iron floc was removed by filtration; thereby eliminating the interference and resulting in a stable ortho-phenanthroline color.

The effect of time on bathophenanthroline color is shown in Table 10. In contrast to the ortho-phenanthroline color, the bathophenanthroline color shows slight decreases in the apparent ferrous iron with time. In this case, since the ferric iron was eliminated upon extraction, the colored solutions which consisted largely of ferrous iron may have been oxidized to ferric iron in order to shift toward equilibrium condition which resulted in a fading of the color with time. However, the changes in color of bathophenanthroline were relatively small in comparison to those occurring with ortho-phenanthroline.

The results shown in Table 11 indicate that the "ortho-phenanthroline only" method, followed by membrane filtration within 10 minutes after being fixed, is very comparable to the bathophenanthroline method. In addition, this experiment indicates that some organic and other interfering substances which might be present in raw water do not seem to show any interference with the ferrous iron determination, since the iron content of the mixture obtained experimentally agreed quite well with the corresponding calculated value which is the sum of the iron in the raw water and the standard solution. However, there is a question which still has to be resolved, as to whether the apparent ferrous iron as obtained in the raw water represents all the ferrous iron present. It is also possible that the ferrous iron which was revealed in the raw water might represent only that portion which was not complexed with organic matter and other interfering substances. Lee and Stumm (31) recommended boiling the original samples with hydrochloric acid when determining ferrous iron in natural water by the bathophenanthroline method, in order to free the chelated or complexed iron. However, it is possible that boiling the sample with acid will change the original ratio of the ferrous-ferric iron in the sample.

A further modification of the "ortho-phenanthroline only" method was employed by filtering samples through the Whatman No. 40 filter paper and comparing the results with the membrane filter and the bathophenanthroline method. Filter paper was employed in order to see whether it could be used as a substitute for the membrane filter, since the use of paper would not require the use of a vacuum pump which is inconvenient to operate in the field. A period of about 30 minutes was allowed between the time for fixing the samples and the time at which readings were made in the case of ortho-phenanthroline in order to see whether there was any significant change in the stability of the samples when filtered through paper. The results can be compared with those which were obtained by filtering immediately through a membrane filter, since it was previously observed that the color of the solution was stable after being filtered through a membrane filter. It is interesting to note that the method in which the samples were filtered prior to fixing consistently showed the lowest values among the three methods using Whatman filter paper; whereas the method in which the samples were filtered after 30 minutes showed the highest values; and the method in which the samples were filtered immediately after being fixed gave intermediate results. The method in which the samples were filtered prior to fixing also gave values very comparable to both the bathophenanthroline and the method using the membrane filter. It is possible that the method where filtering took place prior to fixing gave the best results because the ferric iron interference was eliminated before the reagents were added. However, in using Whatman filter paper a longer period of time is required for filtration and the possibility of ferrous iron being oxidized is increased. In another experiment, a set of samples filtered through Whatman filter paper were kept for a period of two days under normal laboratory conditions and the colorimetric measurements were again determined.

It was found that the color of the samples increased considerably. Therefore, it can be concluded that Whatman Filter paper is not as effective as the membrane filter in the removal of precipitated iron.

B. Redox Potential Measurements

It should be noted that in a survey study of this type, there are numerous factors in plant operation which vary from plant to plant that cannot be controlled. For example with regards to function efficiency, some plants have a raw water which is highly treatable but due to the failure in operation produces a poor quality water which results in poor overall efficiency. The organic and mineral content of the water also varies from plant to plant. Until now, there are still no simple procedures available for the determination of the various constituents in natural well waters, hence a definite interpretation of the results of redox potential measurements which includes all the various factors is not possible. In this study, the chemical oxygen demand (C.O.D.) of the various waters varied from 1 to 50 mg/l and this was not reduced during treatment. It is possible that these C.O.D. exerting substances may represent the amount of organic constituents which cause chelation and form complexes with iron, postulated by many investigators. From the plot presented in Fig. 5, it appears that raw waters having a high redox potential in general were low in C.O.D. and vice versa.

Another factor which also affected the results of this study was the lack of control at the sampling points in the plant. For example, in some plants the raw water could be collected directly from the well head; but in some cases raw water at this point was unobtainable and the raw water from storage was used instead. This water might not represent the actual characteristics of the raw water because of the possible addition of atmospheric oxygen and other substances to the water during storage, thereby changing the actual characteristics of the raw water. The sampling

points after aeration also varied from plant to plant. In some plants the aerated water was available right after the aeration process, and in some plants the aerated water could not be sampled until at the top of the filters. In the latter case, the water usually had been retained in a reaction tank for a period of about one hour, which would allow a greater degree of oxidation than if the water had been sampled immediately after aeration. In the experiments performed in the laboratory with natural and synthetic waters, it was found that both oxidized iron and redox potential increased gradually with time following aeration; therefore, sampling time after aeration must also be taken into consideration in order to compare the characteristics of the raw waters in their response to aeration. The redox potential measurements made in this study were quite reliable within a reasonable range of precision since the measurements were made by the use of two duplicate platinum electrodes and the values agreed within 20 mv. The electrodes were also standardized using a quinhydrone standard solution. The results are given in Appendix A. The maximum difference between the extreme values obtained by the two electrodes were within 20 mv and the maximum differences from the standard values were within $\pm$ 10 mv. In some cases when water contained a high gas concentration, the meter reading became sluggish and a reliable reading was difficult to obtain. Rinsing the electrodes in concentrated sulfuric acid greatly improved the readings in all cases. A correction factor for the raw water of 80 mv per pH unit as obtained by calculation from the results of this survey was used instead of 60 mv per pH unit which is the widely accepted standard correction. Regardless of whatever factor is employed, the differences of the correction was not greater than 10 mv in most cases. It is interesting to note that the average computed correction factors of both the aerated and the finished water was 60 mv per pH unit which is equal to the standard correction factor.

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However, these were averages from values ranging from 40 to 86 mv in the case of aerated water, and from 34 mv to 83 mv in the case of finished water. No doubt some values were the results of some experimental errros in the measurement. As Baas and others (6) indicate, the correction of redox potential per unit charge in pH depends very largely on the species of iron present and ranging from 59 mv to 237 mv according to their illustrations. The direct effect of dissolved oxygen alone on the redox potential reading was not significant as observed in both laboratory and field experiments. The treatment plant at Edwardsville, for example, the measurement of redox potential of aerated water was made almost immediately after aeration. The increase in redox potential was found to be only 30 mv whereas the increase in dissolved oxygen was 7.8 mg/l. Baas and his associates (6) had noted from the results of their experiments that the variation in the molecular oxygen content of water appeared to have no direct influence on the electrode potential, except at very low oxygen tensions. The presence of small amounts of oxidizable matter, both organic and inorganic would, however, be reacted on by the molecular oxygen; this could poise the system at a lower E_h. The effect of dissolved oxygen on natural raw water hence can be explained similarly.

It was not the purpose of this study to develop a definite quantitative relationship between the amount of ferrous or ferric iron remaining and the redox potential. Theoretically this is not possible, since redox potential only indicates the relative ratio of the amount of oxidants to reductants, which in this case would include all reduced and oxidized organic and mineral substances besides iron. However, it may be possible that redox potentials can be used empirically to indicate the ranges and oxidation stages of water in a manner similar to the application of redox potentials in other fields. The changes in redox

potential may help to indicate the relative ranges of oxidation attained.

From the results shown in Table 14, the changes in redox potentials resulting from aeration varied from +370 to +70 mv. The changes in redox potentials from raw to aerated water, however, increased gradually with time following aeration. Since the sampling points varied from one plant to another plant, the elapsed time after aeration was not equal. Hence, the redox potentials of various plants with respect to their response to aeration should not be compared due to the fact that the redox potentials change with time. An attempt was made to correlate the changes in redox potentials to the corresponding changes in ferrous and ferric iron at various stages of treatment. From the results shown in Table 14, a general trend is observed since when the change in redox potential is high, the corresponding increase in the percent of oxidized iron or the percent decrease in ferrous iron is also high. It appears that a change in redox potential of +150 mv was a limit above which the increase in the oxidized iron (or the decrease in ferrous iron) generally would be above 60 percent, and below which the increase in the oxidized iron would be less than 60 percent. Weart and Margrave(50) suggested an increase of +100 mv as a limit for raw water in their response to aeration, above which iron removal would be satisfactory, and below which iron removal would not be satisfactory with conventional treatment. In this survey, there was only one plant where the response to aeration as indicated by redox potential was less than +100 mv and the effluent was not satisfactory. There were many palnts which showed increases in redox potential above +100 mv, and where the treatment still was not satisfactory. It would seem, however, that the response of water to aeration is not adequate to be used as a determining factor in the degree of success in treatment since the filter also plays a very important

role in the iron oxidation and removal processes. There were significant changes in redox potentials during filtration which must also be evaluated in determining the efficiency of the treatment, as can be seen from Table 16.

Weart and Margrave (50) also noted that when aeration alone raised the redox potential of a water to a level approaching +244 mv (or 0 mv by calomel electrode), the plant would function satisfactorily if reasonable care was given to its operation. From the results of this survey as shown in Table 13, there were six plants with no chlorine which had an aerated water redox potential less than or equal to 250 mv (or 0 mv by calomel electrode). Results at these plants were not satisfactory. Hence, the results of this survey confirm the previous findings.

For the group of waters, which were chlorinated, there was a general trend in that the increase in redox potential at every stage related closely to the increase in the residual chlorine irregardless of the changes in ferrous or ferric iron. This can be related to the fact that chlorine is a strong oxidizing agent.

The changes in redox potentials from raw to finished waters seemed to be a very good measure of the overall iron removal efficiency. It can be observed from Table 15 that a redox potential increase of +200 mv is a limit, below which the treatment was not satisfactory. For thirteen plants where an increase in redox potential of less than 200 mv was observed, there was only one case (Broadlands) in which the total iron remaining in the effluent was less than 0.2 mg/l; and two cases (Walnut and Argenta) where the total iron remaining was lower than 0.4 mg/l; whereas the other ten plants had greater than 0.4 mg/l of total iron remaining in the finished water. Hence, the measure of increase in redox potential from the raw to the finished water was a better measure of the effectiveness of treatment than the change in redox potential from the raw to the aerated water.

However, for those nine plants which no chlorine and where the increase in redox potential was greater than +200 mv, there were two (Roxana and Oakwood) whose effluent proved to be unsatisfactory. In both these plants the ratio of total iron to ferrous iron remaining was higher than in other plants within the same group. Since the redox potential is the measure of the ratio of the oxidants to the reductants, the presence of a high ratio of total iron to ferrous iron might effect a high redox potential reading. However, it is liekly that there was an improper functioning of the filters involved since it is very unusual for a normal filter to have a concentration of total iron in the effluent greater than five times that of the ferrous iron concentration. In the case of Roxana, there appeared to be a break through in the filter since the concentration of iron in raw water was unusually high (over 15 mg/l). Because Oakwood was also having particular problems with its filters, these two plants should be regarded as exceptions.

From the results shown in Table 16, no correlation can be drawn between the changes in redox potential across the filters and changes in other characteristics. However, it was noted that for all plants (including both those with and without chlorine) with a decrease in potential over -80 mv during filtration, the degree of success in the treatment was very poor. All plants which showed an increase in ferrous iron during filtration are included in this group. It is interesting to note that in the case of La Moille, there was a large decrease in redox potential (-330 mv) across the filter which corresponded to the increase in the ferrous iron concentration and a depletion in residual chlorine.

An increase of redox potentials resulting from filtration however, did not always accompany successful treatment. In almost all plants, with and without chlorine, there was a depletion of oxygen during filtration

and a corresponding increase in the nitrate concentration. Weart and Margrave (50) have pointed out that such a depletion in dissolved oxygen during the passage of water through a filter was a sure indication of the existence of an extremely active biological flora and fauna. In what way and to what extent, this biological growth has effect on the filter is not yet understood. The reduction in oxygen across the filters for chlorinated water was in general less than that for unchlorinated water. This may have been due to the fact that chlorine is a disinfectant which may have diminished the biological growth in the filters. Another question which is often raised concerns whether the dissolved oxygen introduced during treatment is a factor which limits the success of the treatment. Theoretically, only 1.4 mg/l of oxygen will be required to oxidize 10 mg/l of the ferrous iron. From this plant survey, it can be seen that the dissolved oxygen in the aerated water in almost all plants exceeded 7 mg/l, whereas the ferrous iron was less than 5 mg/l in most cases and over 50 percent of this already had been converted to the ferric iron form during aeration. Hence, it can be concluded that in the plants studied the dissolved oxygen was sufficient and was not a limiting factor. It is also obvious that the depletion of oxygen in the filter was not entirely due to the oxidation of iron.

From the results shown in Table 17, it appears that there is a general correlation between the redox potentials and the amount of ferrous and total iron remaining in water with no chlorine; at high redox potentials both the ferrous iron and total iron remaining were generally low and vice versa. It can be seen that for all finished waters which had a redox potential less than 270 mv treatment was not satisfactory since the iron remaining exceeded 0.4 mg/l; whereas for those finished waters with redox potentials higher than 270 mv which included thirteen plants, nine exhibited a satisfactory finished water quality while four plants did not. Among

these four plants, the percent of ferrous iron was less than 30 percent. This limit of 270 mv can be very well applied empirically to most plants not using chlorine under normal operating conditions where the ferric iron is being effectively removed on the filters. For those plants using chlorine, there was no correlation between the redox potentials and either ferrous or ferric iron content. The redox potential however, does show a good correlation with the residual chlorine.

From the plot of the redox potential against the C.O.D. of each raw water, it is apparent that the waters tested can be separated quite distinctly into two groups with respect to their treatability for iron removal. The group of waters which contain less than 0.2 mg/l iron in the plant effluent fall in the "Zone of Highly Treatable Quality". This corresponds to the region of C.O.D. ranging from 0 to 20 mg/l where the redox potential is above +150 mv. Those plants in which the effluent contained iron in quantities greater than 0.4 mg/l fall in the "Zone of Poorly Treatable Quality" which corresponds to the area of C.O.D. greater than 20 mg/l with the redox potential below 120 mg. It is possible that the redox potentials alone could be used to determine a water's respone to treatment in a manner similar to the application of redox potentials in determining the corrosiveness of soils as suggested by Starkey and Wight (47). In the case of water, it can be concluded from the results of this study that a raw water which shows redox potentials higher than 150 mv will respond very well to treatment by the conventional methods, and those which show redox potentials less than 120 mv will not readily respond. If it is possible to predict the response of the raw water to treatment by this simple method, this measurement may be very useful in the treatment plant design. Proper adjustments can be made later within a plant to make it more efficient.

Since many aspects of water treatment are similar to waste treatment, it may be possible that redox potential measurement can be applied to the treatment of water in the manner similar to that being used in the waste treatment. The similarity between the water treatment and the waste treatment is shown in Fig. 6. From the results obtained in this study, it can be seen that the initial redox potential of raw water was relatively low just as a raw waste. Upon aeration or oxidation by chlorine, the redox potential was increased. When water passed through a filter, the redox potential would either increase or decrease (as the results show in Table 16). If there was a large drop in redox potential across the filter over a certain limit (-80 mv as indicated from the results of this investigation), it indicated an abnormal condition of the filter, perhaps indicating that the filter should be backwashed. If the redox potential of the effluent was lower than 270 mv, as observed from this study, it indicated a poor quality effluent. This is very similar to waste treatment where, when the redox potential of the effluent decreases to about -100 mv. it is an indication of the start of unsatisfactory plant functioning. The application of redox potentials as an automatic control has been successfully incorporated into both industrial and domestic waste treatment (25, 45, 49). It is possible that a similar technique can be applied to water treatment. The same limits may not be applicable in all plants, however, but by comparing the results of redox potential measurement to the chemical analysis at a particular plant over a period of time, an accurate and reliable limiting range of redox potentials can be established for that plant. One of the great advantages of water over a waste is that the characteristics of the well water is normally more consistent and usually does not change over a period of years, whereas a waste is normally highly variable in its characteristics.

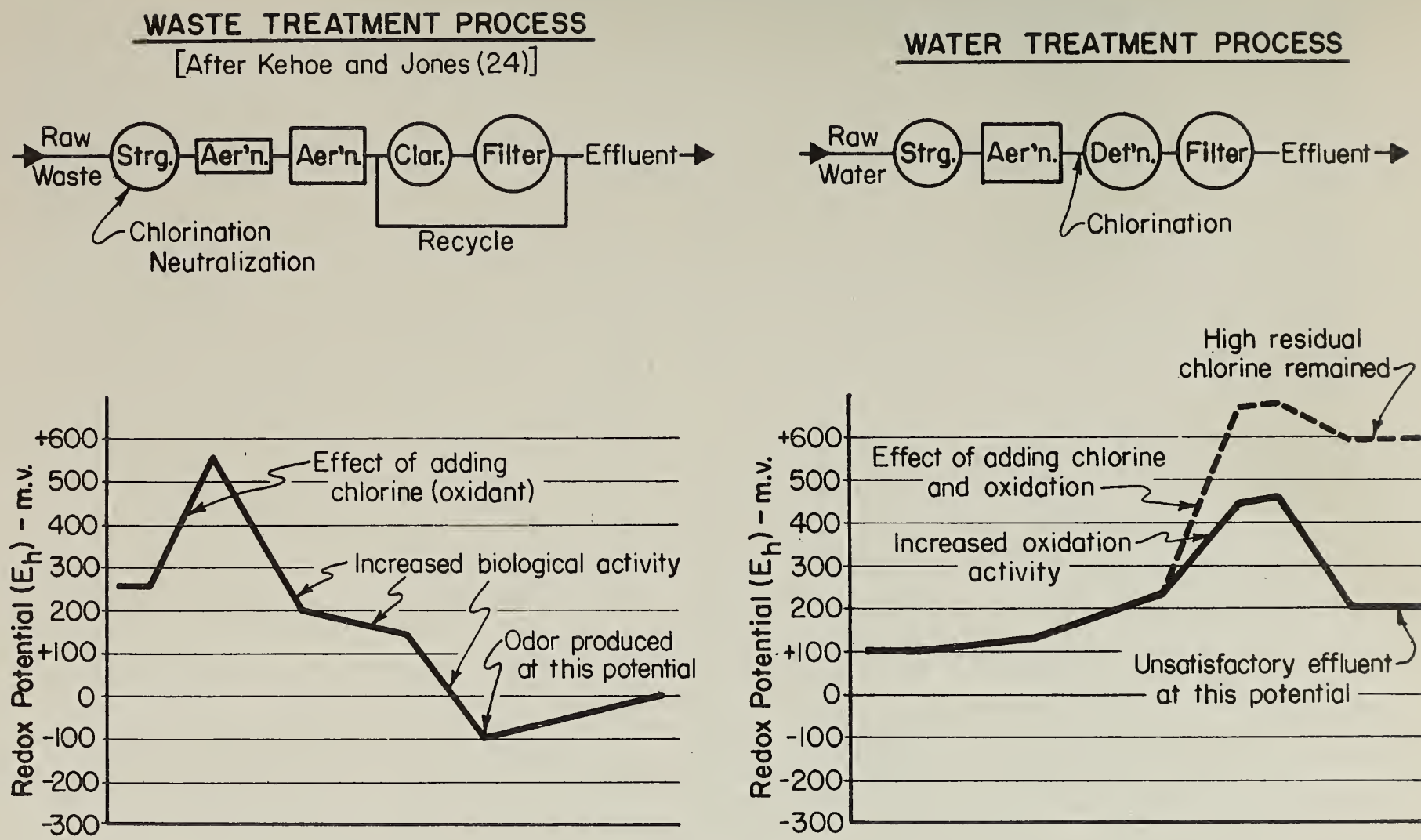

Figure 6

SIMILARITY OF GROUND WATER TREATMENT TO WASTE TREATMENT IN REDOX POTENTIAL - APPLICATION

VII. CONCLUSIONS

A. Methods of Analysis of Ferrous Iron

1. The bathophenanthroline method has proved to be very sensitive in the determination of both ferrous and ferric iron. The ferrous iron can be determined accurately even in the presence of a large amount of ferric iron. This method therefore can be regarded as a reference method. The bathophenanthroline color complex was found to decrease with time resulting in lower values of ferrous iron if the colorimetric determination was delayed.

2. The presence of ferric iron in the sample interferes with the determination of ferrous iron by the ortho-phenanthroline method. The erros increases as the ratio of ferric to ferrous iron increases.

3. The total iron can be determined with accuracy and reliaility by the ortho-phenanthroline (11th Edition Standard Methods) regardless of the species of iron.

4. The method of determining ferrous iron by ortho-phenanthroline with ammonium or sodium acetate buffer generally gives values for ferrous iron which are higher than both the calculated and the bathophenanthroline values, especially when the ratio of ferric to ferrous iron is high. In methods where samples are first acidified then buffered similar results are obtained.

5. The turbidity caused by the precipitated iron interferes with the determination of ferrous iron by ortho-phenanthroline. Its effect can be offseted by using an adjusted blank or by filtration of the samples.

6. The "ortho-phenanthroline only" method will give results closest to the bathophenanthroline method as compared with the other ortho-phenanthroline methods employed.

7. The samples after being fixed with ortho-phenanthroline in the determination of ferrous iron in the presence of ferric iron are not stable and gradually change with time. This is also true of the method using acetate buffer as recommended in the 11th Edition of Standard Methods. The percent increase becomes larger as the ratio of ferrous to ferric iron decreases. However, if the sample is filtered immediately after being fixed through a membrane filter, the color becomes quite stable. No significant change is observed even after a period of 3 days. If Whatman Filter paper (No. 40) is used instead of a membrane filter, the precipitated iron is not completely removed and a significant change in the color of the solutions can be observed with time.

8. The method of filtering with Whatman filterpaper prior to fixing with ortho-phenanthroline will also give values comparable to the bathophenanthroline and the membrane filter method. In this case the precipitated iron is removed from the solution which prevents its reaction with ortho-phenanthroline. This modification may prove to be an effective means of determining ferrous iron in the presence of large quantities of precipitated iron provided that filtration can be done in a short period of time such that the oxidation of ferrous iron prior to being complexed with ortho-phenanthroline is prevented. Filtration with Whatman filter paper is not as effective as the membrane filter in the removal of precipitated iron.

9. The "ortho-phenanthroline only" method can be employed satisfactorily in the determination of ferrous iron by providing one of the following modifications:

a. Using the corresponding adjusted blank which consists of a proportional volume of the sample and distilled water, and making the colorimetric measurement within 10 minutes.

b. Filtering the fixed samples through a membrane filter immediately after fixing with ortho-phenanthroline. The colorimetric measurement then can be made against a distilled water blank. Filtration of samples into ortho-phenanthroline reagent may also be applicable provided that filtration is finished within a very short period of time.

B. Redox Potential Measurements

On the basis of the investigations reported herein, it is possible to draw the following conclusions:

1. The redox potential measurement can be a useful tocl in determining the efficiency and controlling the treatment process with respect to iron removal.

2. The redox potential and chemical oxygen demand of raw water can be used to characterize their qualities in response to the treatment by conventional process. This could prove to be very useful in treatment plant design. It was found that raw water with redox potentials higher than +150 mv and chemical oxygen demands less than 20 mg/l were highly treatable; waters with redox potentials lower than +120 mv and C.O.D. higher than 20 mg/l did not respond very well to treatment. It is also possible that the above characteristics could be distinguished by the use of redox potentials only.

3. There is a general correlation between the change in redox potential and the percent increase in oxidized iron in the aerated water with no chlorine. A redox potential increase of +150 mv was a general limit above which the corresponding increase in oxidized iron would be above 60 percent of the total iron and below which the increase in oxidized iron would be less than 60 percent.

For the aerated water with chlorine, the increase in redox potential agreed closely with the increase in the residual chlorine without regard

to changes in ferrous or ferric iron.

4. The increase of redox potential from raw to finished water is a good parameter in determining the success of the treatment; an increase in the redox potential of less than +200 mv indicated unsatisfactory plant performance; and an increase above +200 mv indicated satisfactory performance with few exceptions.

5. The sharp decrease in redox potential during filtration is an indication of a reducing condition within the filter. A decrease of potential over -80 mv, indicated an improper functioning of the filter which is often followed by the depletion of oxygen. In some filters the ferric iron is again reduced to the ferrous form. However, an increase in the redox potential during filtration did not guarantee the satisfactory performance of the filter.

6. There is a general correlation between the redox potentials and the amount of ferrous and total iron remaining in the finished water where no chlorine was added; at high redox potential the iron remaining is generally low; and vice versa. It was found that all finished waters having redox potentials less than 270 mv showed a total iron concentration greater than 0.40 mg/l and those whose redox potentials exceeded 270 mv showed satisfactory quality under normal operating conditions where the ferric iron is being effectively removed on the filters.

7. It is conceivable that redox potential measurements could be incorporated into the water treatment process as an automatic control device in the manner similar to those being used in the treatment of waste water. It may be used in maintaining the oxidation level required for satisfactory performance and to regulate frequency of back-washing the filters.

At the present time it is not possible to apply a definite theoretical interpretation to the redox potential, since the various influencing factors involved are still not evaluated. However, the redox potential may be used empirically at a particular plant by correlating it with the chemical anlysis obtained over a period of time for different operating conditions.

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APPENDIX A

STANDARDIZATION OF REDOX POTENTIAL ELECTRODES WITH STANDARD QUINHYDRONE*1 - BUFFER SOLUTIONS

Temperature range	Extreme values of Observed Potentials - mv.			Standard*2 Potentials - mv.	
	25°C	to	20°C	20°C	25°C
pH 7.0 Buffer Solution *3	53	to	38	47	41
pH 4.0 Buffer Solution *4	240	to	219	223	218

*1 Quinhydrone - Fisher Reagent Chemical (Cat No. Q5), Fisher Scientific Co., Fair Lawn, New Jersey

*2 According to Kehoe (24), these readings are the ones most pH and millivolt meters indicated.

*3 Reference Buffer solution produced by Leeds and Northrup Co.

*4 Reference Buffer solution produced by Beckman Instruments, Inc.

The above result shows the comparison of the potentials observed from the electrodes employed to the standard potentials in the quinhydrone-standard buffer solutions. The observed values shown are the extreme values which constitute the range of the observed values as obtained by various combinations of the platinum and calomel electrodes employed at various times throughout this study. The standard values are obtained from a presentation by Kehoe (24), in which he claimed that these values are the ones most pH and millivolt meters indicated and adopted as standard values. It can be seen that the electrodes employed gave quite good agreement with the standard values, even the extreme values lie within the range of allowable erros in the redox potential reading.

APPENDIX B

COMPUTATION OF REDOX POTENTIAL CORRECTION FACTORS IN RELATION TO pH

Raw Water

Town	Natural		Acidified		Δ pH	Δ ORP	Δ ORP/Δ pH
	pH	ORP mv.	pH	ORP mv.		mv.	(mv./pH unit)
Warrensberg	7.00	140	1.00	690	6.0	550	92
Argenta	7.50	90	1.00	658	6.5	568	87
Cisco	7.00	120	1.00	650	6.0	530	89
Broadlands	7.50	160	1.00	680	6.5	520	80
Fairmount	7.35	130	1.00	660	6.35	530	84
Oakwood	7.50	110	1.00	650	6.5	540	83
St. Joseph	7.50	150	1.00	650	6.5	500	77
Tolono	7.50	310	1.00	720	6.5	410	63
Arcola	7.50	210	1.00	680	6.5	470	73
Atwood	7.10	150	1.00	680	6.1	530	87
Bethany	7.20	70	1.00	630	6.2	565	91
Findlay	7.20	100	1.00	650	6.2	550	89
Windson	7.00	130	1.00	720	6.0	590	93
Deland	6.70	130	1.00	610	6.7	480	72
Wapella	6.85	90	1.00	570	6.85	480	70
Heyworth	7.30	170	1.00	610	6.3	440	70
Roxana	6.80	80	1.00	550	6.8	470	69
Edwardsville	7.10	130	1.00	680	6.1	550	90
Marine	7.40	70	1.00	580	6.4	510	80
Mahomet	6.90	170	1.00	630	6.9	460	67
Forrest	8.00	-100	1.00	650	7.0	750	108
Chatsworth	7.45	-	1.00	670	6.45	-	-
Emden	7.10	110	1.00	620	6.1	510	84
Tremont	6.90	110	1.00	640	5.9	530	90
Morton	7.30	70	1.00	630	6.3	560	89
Wyanet	7.40	90	1.00	640	6.4	550	86
Walnut	7.25	170	1.00	650	6.25	480	77
La Moille	7.35	130	1.00	610	6.35	480	76
Danvers	7.40	50	1.00	550	6.40	500	78
Hudson	7.30	70	1.00	530	6.30	460	73
El Paso	7.10	180	1.00	650	6.10	470	77
						Σ	2444
						30	

$$\text{Correction Factor} = \frac{2444}{30} \simeq 80$$

mv./unit pH

APPENDIX B (Continued)

Aerated Water

Town	Natural		Acidified		Δ pH	Δ ORP	Δ ORP/Δ pH
	pH	ORP mv.	pH	ORP mv.		mv.	(mv./pH unit)
Warrensberg	7.50	640	1.00	990	6.50	350	54
Argenta	7.60	260	1.00	690	6.60	430	65
Cisco	7.20	220	1.00	700	6.20	480	78
Broadlands	7.55	310	1.00	730	6.55	420	64
Fairmount	7.40	-	1.00	690	6.40	-	-
Oakwood	7.80	340	1.00	720	6.80	380	56
St. Joseph	7.50	490	1.00	750	6.50	260	40
Tolono	7.55	450	1.00	800	6.55	350	54
Arcola	7.60	610	1.00	940	6.60	330	50
Atwood	-	-	-	-	-	-	-
Bethany	7.75	420	1.00	760	6.75	340	50
Findlay	7.55	220	1.00	750	6.55	530	81
Windsor	-	-	-	-	-	-	-
Deland	7.30	290	1.00	690	6.30	400	64
Wapella	7.40	210	1.00	710	6.40	500	78
Heyworth	7.80	280	1.00	660	6.80	380	56
Roxana	7.10	120	1.00	670	6.10	450	74
Edwardsville	7.40	+150	1.00	+700	6.40	550	86
Marine	7.65	+650	1.00	+1050	6.65	400	60
Mahomet	7.35	+420	1.00	+730	6.35	310	49
Forrest	7.10	+390	1.00	+770	6.10	380	62
Chatsworth	7.70	+350	1.00	+730	6.70	380	57
Emden	7.50	+220	1.00	+710	6.50	490	75
Tremont	7.40	+190	1.00	+710	6.40	520	81
Morton	7.70	+610	1.00	+900	6.70	290	43
Wyanet	7.45	+260	1.00	+710	6.45	450	70
Walnut	7.45	-	1.00	+710	6.45	-	-
La Moille	7.90	560	1.00	+970	6.90	410	60
Danvers	7.90	+290	1.00	+700	6.90	410	60
Hudson	7.60	+240	1.00	+670	6.60	430	65
El Paso	8.00	+660	1.00	+1090	7.00	430	62
						Σ	1694
						n = 28	

Correction factor = $\frac{1694}{28}$

$\cong$ 60

mv./pH unit

APPENDIX B (Continued)

Finished Water

Town	Natural pH	Natural ORP mv.	Acidified pH	Acidified ORP mv.	Δ pH	Δ ORP mv.	Δ ORP/Δ pH (mv./pH unit)
Warrensberg	7.50	650	1.00	1020	6.50	370	57
Argenta	7.60	230	1.00	690	6.60	460	70
Cisco	7.10	210	1.00	650	6.10	440	72
Broadlands	7.60	250	1.00	630	6.60	380	58
Fairmount	7.50	350	1.00	770	6.50	420	65
Oakwood	7.80	350	1.00	700	6.80	350	52
St. Joseph	7.55	450	1.00	750	6.55	300	46
Tolono	7.60	200	1.00	730	6.60	530	80
Arcola	7.15	480	1.00	810	6.15	330	54
Atwood	7.40	500	1.00	730	6.40	230	36
Bethany	7.80	405	1.00	750	6.80	345	51
Findlay	7.55	140	1.00	710	6.55	570	82
Windsor	7.25	220	1.00	720	6.25	500	80
Deland	7.35	250	1.00	630	6.35	380	60
Wapella	7.50	110	1.00	650	6.50	540	83
Heyworth	7.80	450	1.00	680	6.80	230	34
Roxana	7.10	280	1.00	670	6.10	390	64
Edwardsville	7.75	540	1.00	900	6.75	360	54
Marine	7.60	670	1.00	1050	6.60	380	58
Mahomet	7.20	430	1.00	730	6.20	300	49
Forrest	7.35	650	1.00	870	6.35	220	35
Chatsworth	7.80	360	1.00	730	6.80	380	56
Emden	7.45	190	7.00	700	6.45	510	79
Tremont	7.55	270	1.00	690	6.55	420	64
Morton	7.70	550	1.00	800	6.70	250	37
Wyanet	7.50	290	1.00	720	6.50	430	66
Walnut	7.45	350	1.00	670	6.45	320	50
La Moille	8.30	200	1.00	680	7.30	480	66
Danvers	7.80	140	1.00	630	6.80	490	72
Hudson	7.70	680	1.00	1090	6.70	410	61
El Paso	7.50	710	1.00	1050	6.60	340	52
						Σ	1843
						n = 31	

Correction factor = $\frac{1843}{31}$

$\simeq$ 60

mv./pH unit

APPENDIX C

RAW WATER CHARACTERISTICS

Town	Temp	pH	D.O.	Ferrous Iron	Total Iron	ORP (E_h)			Corrected C.O.D.
						Natural	Acidified to pH1.0	Corrected to pH 7.0	
	°C	mg/l	mg/l	mg/l	mg/l	mv.	mv.	mv.	mg/l
Arcola	16.5	7.50	0.4	5.02	5.08	+210	+680	+250	22.6
Argenta	13.5	7.50	0.1	1.20	1.36	+90	+658	+130	10.6
Atwood	14.2	7.10	0	2.58σ	2.60	+150	+680	+160	13.8
Bethany	15.0	7.20	0	2.09	2.12	+70p	+630	+90	11.9
Broadlands	13.0	7.50	0.1	1.20	1.44	+160	+680	+200	18.1
Chatsworth	14.0	7.45	0	1.10	1.28	-	+670	-	11.7
Cisco	14.0	7.00	0.3	4.10	4.24	+120	+650	+120	25.1
Danvers	13.8	7.40	0	2.28	2.80	+50	+550	+80	50.4
Deland	13.2	6.70	0	4.58	4.68	+130	+610	+110	48.8
Edwardsville	15.2	7.10	0.6	1.89	2.14	+130	+680	+140	2.8
El Paso	13.0	7.10	0	1.02	1.60	+180	+650	+190	10.4
Emden	13.5	7.10	0	2.60	2.96	+110	+620	+120	9.8
Fairmount	13.0	7.35	0	1.82	1.84	+103	+660	+160	7.3
Findlay	15.2	7.20	-	4.45	4.72	+100	+650	+120	29.5
Forrest	14.0	8.00	0	21.4	26.0	-100	+650	-20	97+
Heyworth	13.0	7.30	0	0.68	0.60	+170	+610	+190	1.0
Hudson	12.8	7.30	0	1.98	2.60	+70	+530	+90	36.2
La Moille	12.3	7.35	0.2	1.50	1.68	+130	+610	+160	12.9
Mahomet	14.0	6.90	0.1	2.00	2.20	+o70	+630	+160	3.8
Marine	13.5	7.40	0	4.18	4.36	+70	+580	+100	37.0
Morton	14.0	7.30	0.8	2.78	3.00	+70	+630	+90	12.0
Oakwood	13.5	7.50	0.6	2.80	3.28	+110	+650	+150	22.9
Roxana	15.2	6.80	0	15.2	16.0	+80	+550	+60	43.6
St. Joseph	14.0	7.50	0	1.78	1.94	+150	+650	+190	9.1
Tremond	13.5	6.90	0	3.42	3.60	+110	+640	+100	12.1
Tolono	16.0	7.50	0	1.78	1.94	+150	+650	+190	9.1
Walnut	12.2	7.25	0.4	2.45	2.64	+170	+650	+190	8.8
Wapella	12.5	6.85	0	4.98	5.00	+90	+570	+80	12.5
Warrensberg	14.0	7.00	0	3.60	3.68	+140	+690	+140	28.1
Windsor	16.0	7.00	0	6.85	8.48	+130	+720	+130	49.4
Wyanet	12.0	7.40	0.20	4.50	4.72	+90	+640	+120	17.8

APPENDIX C (Continued)

RAW WATER CHARACTERISTICS

Town	Residue	Hardness			Alkalinity as $CaCO_3$ *	Chloride	Sulfate *	Nitrate *	Ammonia *	Treatability *
		Ca	Mg	Tot.						
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Arcola	415	203	161	364	366	19.0	33	nil	9.4	C
Argenta	-	183	122	305	418	80	1.2	nil	6	A
Atwood	470	207	150	358	468	2.0	0	nil	1.2	A
Bethany	-	183	154	337	406	25	0	nil	5.2	B
Broadlands	368	135	70	205	344	4.0	3.9	nil	1.7	A
Chatsworth	730	287	201	488	346	0	250	slight	9.1	A
Cisco	658	192	168	360	628	4.0	4.3	nil	11.4	C
Danvers	656	160	130	290	548	54.0	1.2	nil	11.2	C
Deland	655	294	241	535	680	10	0.4	slight	36.0	C
Edwardsville	-	150	72	222	152	2.0	82	high	0	A
El Paso	440	205	147	352	422	0	-	nil	4.9	A
Emden	379	140	150	340	386	3	0	slight	1.9	B
Fairmount	521	230	160	390	292	25	86	nil	0.3	A
Findlay	700	247	153	400	-	25	0	nil	18.0	C
Forrest	480	180	176	356	468	6.0	1.0	slight	0	B
Heyworth	351	-	-	336	280	7	-	slight	5.2	A
Hudson	644	230	195	425	624	0	0.4	nil	8.2	B
La Moille	291	122	93	215	264	1.0	1.0	slight	0	C
Mahomet	-	255	205	460	387	15	96	slight	6.1	A
Marine	571	163	111	274	500	2.0	0.6	slight	4.8	C
Morton	649	172	158	330	414	15.0	2	slight	3.3	A
Oakwood	443	178	127	305	354	13	-	nil	1.7	A
Roxana	410	600	300	900	200	19	106	nil	0.1	C
St. Joseph	388	196	129	325	372	4.0	1.0	nil	1.8	A
Tremont	526	182	228	410	502	2.0	0	nil	1.0	A
Tolono	388	196	129	325	372	4.0	1.0	nil	1.8	C
Walnut	302	178	127	305	310	0	0	nil	1.2	A
Wapella	410	206	146	352	410	4.0	0	slight	2.0	C
Warrensberg	527	170	140	310	422	8.0	0	nil	9.0	C
Windsor	-	217	180	397	630	7.0	11	slight	13.4	C
Wyanet	495	222	158	380	440	6.0	0	nil	2.8	C

* Data shown in these columns was obtained from "Mineral Examination of Water" data of Sanitary Engineering Laboratory, Department of Public Health, Springfield, Illinois.

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